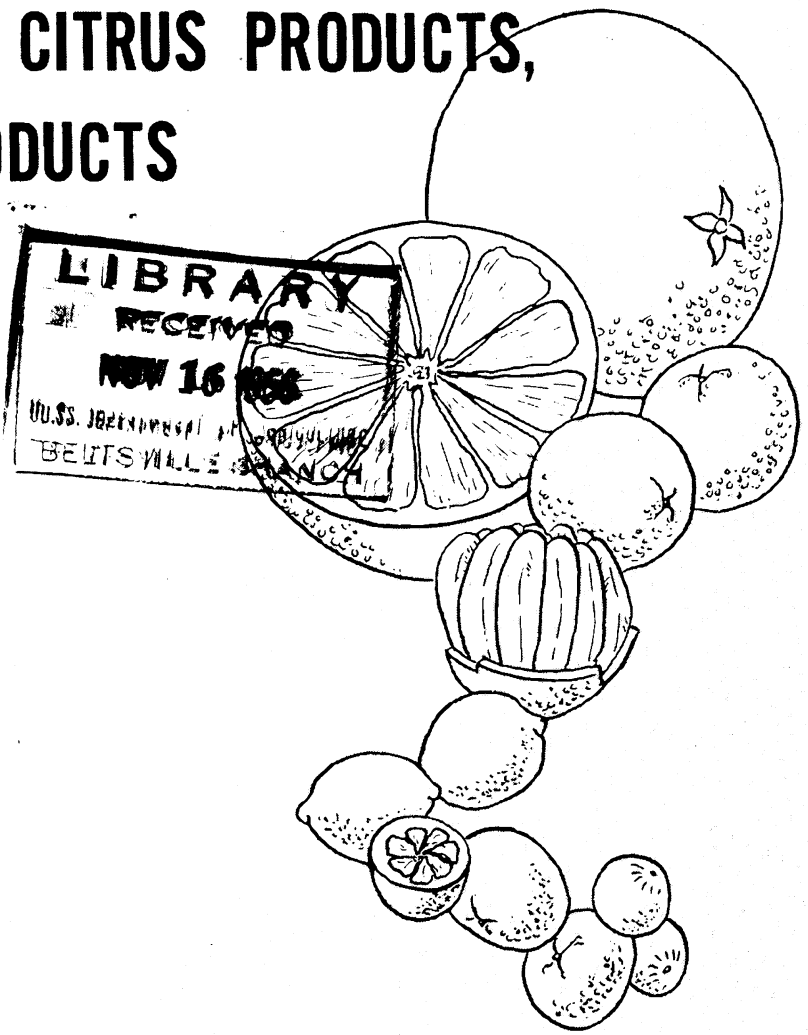
AGRICULTURE HANDBOOK NO. 98 NOVEMBER 1956

CHEMISTRY AND TECHNOLOGY OF CITRUS, CITRUS PRODUCTS, AND BYPRODUCTS



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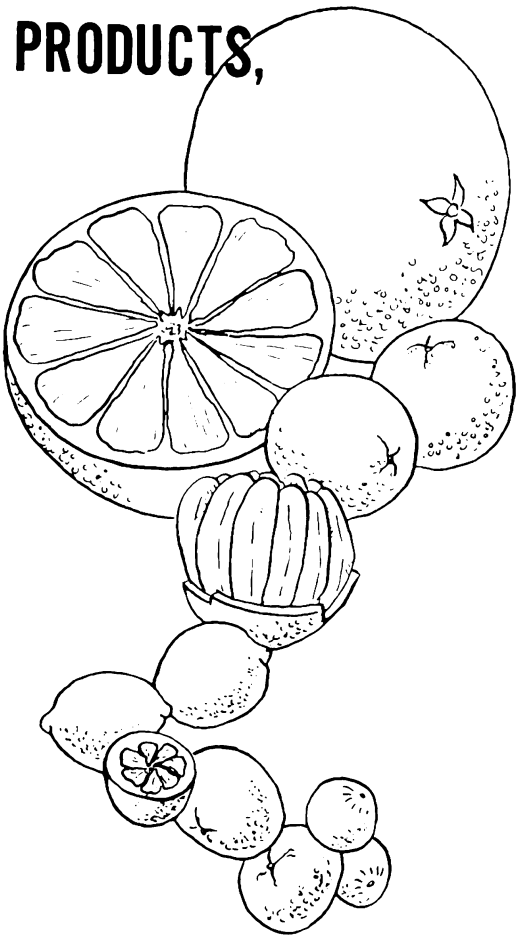

Prepared by the
AGRICULTURAL RESEARCH SERVICE

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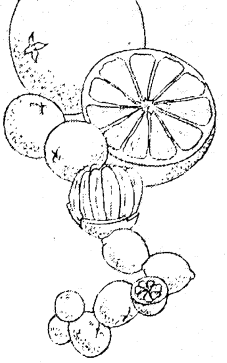
CHEMISTRY AND TECHNOLOGY OF CITRUS, CITRUS PRODUCTS, AND BYPRODUCTS [1]



Prepared by the
AGRICULTURAL RESEARCH SERVICE [2]

Production of citrus in the United States has increased from about 174 million boxes in 1943 to slightly less than 200 million boxes in 1955. Increasing attention is being given to the processing and utilization of citrus other than for the fresh-fruit market in order to effectively market the ever-expanding production of citrus fruit.

In the early 1930's the principal fruit used for processing consisted of culls from fresh-fruit packinghouses. This fruit was sound, but because of offsize or peel blemishes was not considered suitable for the fresh-fruit market. Processing of these culls into citrus products added to the returns of the grower. During the 1953-54 season 43 percent of the oranges, 51 percent of the grapefruit, and 53 percent of the lemons grown reached the fresh-fruit market. The remaining percentage was processed by canning or freezing, or was made into preserves, citric acid, pectin, oil, or feed. In a few years processing has progressed from a means of utilizing culls to becoming the backbone of the citrus industry. Figure 1 shows a citrus-products plant.

The purpose of this handbook is to describe the latest methods for processing citrus products and byproducts. These methods are the results of researches by the United States Department of Agriculture, State experiment stations, and private industry.

In carrying out most of the operations described, competent technical aid is necessary, and the economic situation, both local and national, should be adequately investigated before considering commercial operations.

STRUCTURE AND COMPOSITION OF CITRUS FRUITS

The demand for and acceptance of citrus fruits in the daily diet of human beings is based largely on their nutritional value, flavor, aroma, and other esthetic characteristics, such as color and texture. These quality factors are dependent directly on the structure and chemical composition of the fruit. Citrus fruits are a primary source of our daily requirement for vitamin C, and, in addition, supplementary nutritional value is obtained from the amino acids, inorganic salts, carbohydrates, and probably other still unidentified factors present in the edible portion of the fruit. The color of the fruit is derived from carotenoid pigments, chlorophyll, and possibly flavonoids. The characteristic aroma is obtained from the volatile essential oils found in the peel. All these chemical constituents plus many others present in smaller quantities are the result of the combined influences of genetic regulatory mechanisms and the physical, chemical, and biological environments to which the fruits are subjected during growth and after harvest. Table 1 summarizes the chemical composition of orange juice.

[1] Supersedes Circular 577, Citrus Fruit Products.

[2] Contributors were E. A. Beavens, G. J. Keller, J. G. Kirchner, R. J. McColloch, J. M. Miller, R. G. Rice, L. B. Rockland, and J. C. Underwood, chemists, and E. R. Wolford, bacteriologist, of the Western Utilization Research Branch; O. W. Bissett, T. J. Kew, W. C. Scott, L. J. Swift, and M. K. Veldhuis, chemists, of the Southern Utilization Research Branch; and H. W. von Loesecke, chemist, of the former Washington Utilization Research Branch.

FIGURE 1.—Aerial view of a Florida citrus-products plant. (Courtesy of Minute Maid Corp., Plymouth, Fla.)

TABLE 1.—*Approximate chemical composition of orange juice*

Class of constituents	Constituents	Total soluble solids
	Number	*Percent*
Carbohydrates	7	76.0
Organic acids	7	9.6
Amino acids, free	17	5.4
Inorganic ions	14	3.2
Vitamins	14	2.5
Lipid constituents	18	1.2
Nitrogen bases and glutathione	5	.9
Flavonoids	1	.8
Volatile constituents	33	.38
Carotenoids	22	.013
Enzymes	12	
Total	150	[1]100

[1] Approximate.

In fresh citrus fruits the many chemical constituents and enzyme systems, conservatively estimated at several hundred, are so located in different cells, tissues, and other portions of the fruit that they are able to perform their physiological functions without interfering or reacting with one another. However, when the juice is extracted from the fruit by crushing, pressing, or reaming, these multitudinous constituents are mixed together where they may react to bring about undesirable changes in flavor, color, and aroma. In order to maintain maximum quality in processed citrus products, it is essential that we know what chemical constituents are present in citrus fruits, how they react with each other, and how their reactions may be controlled.

Macroscopic and Microscopic Structure (Fig. 2)

Citrus fruits are covered with a rind, or peel, to protect the pulp, or edible portion, of the fruit. The rind is made up of a cuticle on the outside, thinly covering an epidermal layer (flavedo) containing numerous oil sacs, or glands, filled with an aromatic essential oil having commercial value (p. 62). In addition to these oil sacs, the flavedo contains coloring matter, which is not uniformly distributed

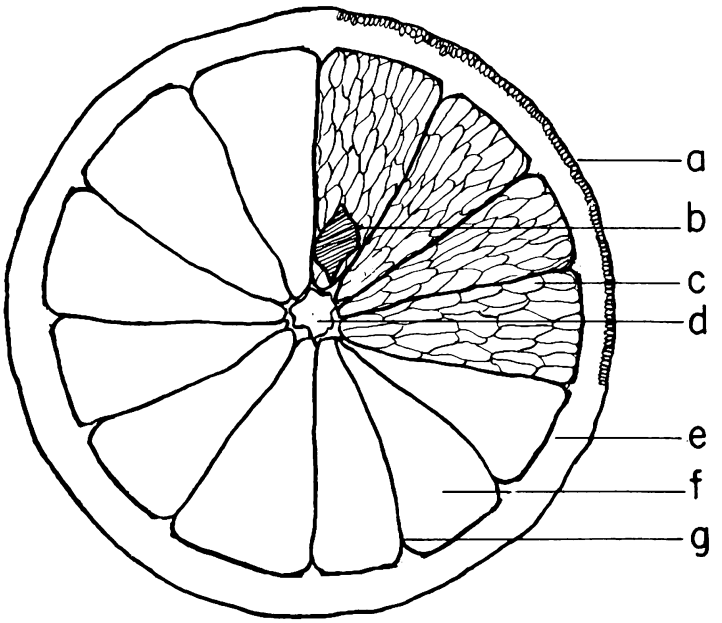


FIGURE 2.—Schematic view of the cross section of an orange: *a*, Oil sacs in flavedo; *b*, seed; *c*, juice sacs; *d*, center core; *e*, albedo; *f*, segment; *g*, segment membrane.

throughout this layer but is concentrated in minute bodies called chromatophores, green in young fruit and gradually turning yellow or orange as the fruit matures (*291*).[3]

A white spongy portion of parenchymatous cells, known as the albedo, lies directly beneath the flavedo. The cells of this spongy layer are loosely arranged with large intercellular spaces and are irregular in shape. This layer contains approximately 20 percent of pectinous substances, which can be recovered in the form of citrus pectin (p. 53).

The inner pulp or flesh of the fruit consists of segments (locules), separated by a membrane of thin epidermal tissue and containing numerous spindle-shaped juice sacs (vesicles) and seeds. The juice sacs in each segment are attached to the segment wall and in contact with the peel by means of fine threads of varying length. Embedded within the cellular tissue in the central part of each juice vesicle are oil droplets (*90*). Yellow chromatophores of crystalline origin may be observed when these juice sacs are crushed and examined microscopically (*277*).

The central axis (core) of the fruit is composed of a white spongy tissue similar to that found in the albedo. The core and segment membranes are collectively called the "rag" of the extracted juice.

[3] Italic numbers in parentheses refer to Literature Cited, p. 81.

Nitrogenous Constituents

The nitrogen content of whole citrus fruits varies between 0.1 and 0.2 percent on a wet-weight basis (*54*). However, the nitrogenous constituents in citrus-fruit juices compose from 5 to 10 percent of the total solids. Those known to occur in citrus fruits include proteins, simple peptides, amino acids, betaines, phosphatides, and related substances. These classes of constituents are normal metabolites of both plant and animal tissues, and contribute to the nutritional value of those plant and animal products used for food and feed. Evidence has indicated that amino acid-sugar (*260*) interactions may be important in the darkening and development of off-flavors in citrus (*438*) and other food products (*87*).

The proteins in citrus fruits are relatively insoluble, and are found to be associated with the solid portions of the fruit, such as the seeds, flavedo, albedo, chromatophores, and pulp. Amino acids are found in the juice of the edible portion of the fruit and in the aqueous alcohol extractable fraction of the peel.

Until recently very little systematic work had been done on the determination of the nature, amounts, and reactivities of the nitrogenous constituents in citrus fruits, primarily because of the unavailability of satisfactory analytical procedures. During the past few years a number of new methods have been evolved for estimating amino acids and other

nitrogenous constituents in biological fluids. One of the most rapid and convenient of these new techniques, called filter-paper partition chromatography, has been particularly useful for both qualitative and quantitative estimations of amino acids in citrus juices and hydrolyzates of proteins extracted from the solid portions of citrus fruits.

Several of the free amino acids have been found in the juice in amounts comparable to the vitamin C content. Asparagine and glutamine were detected in the orange as early as 1908 (*385*) and later in lemon juice (*406*). In 1913 three nitrogenous constitutents—$C_9H_{18}N_2O_6$, $C_6H_7N_3O_2$, and $C_8H_{15}NO_2$—were isolated from lime juice (*125*). However, the formulas do not correspond with any of the known constituents in citrus juices. Betaine and stachydrin were isolated and identified in orange juice by Yoshimura in 1918 (*184, p. 169*). These two constituents and putrescine were also isolated from the pummelo in 1927 (*184*); putrescine was later isolated from orange juice (*173*). Florida Valencia orange juice was found to contain arginine, aspartic acid, and choline (*316*), in addition to asparagine and stachydrin, whose presence had been known earlier. A small amount of free histidine has also been reported (*316, 438*). Choline and a compound presumed to be ethanolamine were isolated from the lipid fraction of Florida orange juice in 1951 (*426*).

The development of filter-paper chromatography techniques has facilitated the systematic estimation of nitrogenous constituents in a wide variety of citrus juices and in the tissues of California Valencia oranges. Cysteine and the simple tripeptide glutathione have been isolated from Valencia and Washington Navel orange juice (*203*), and estimated as the free, reduced compounds in fresh and heated juices from grapefruit, lemon, lime, and orange (table 2). Significant losses of aspartic acid, serine, glutamic acid, and alanine in heated California Valencia orange juice have also been observed (table 3). However, no qualitative changes were observed in free amino acids during the normal "browning" of California Valencia and Washington Navel orange juices (*434*). The free amino acids have been characterized in the juices of 6 commercial and 5 hybrid varieties of citrus grown in California, including Valencia orange, Washington Navel orange, tangerine, grapefruit, lemon, lime, Dweet tangor, and Kara, Kinnow, and Honey mandarins, and a lemon-orange hybrid (*438*).

The quality of the free amino acids and of related constituents in citrus juices appears to be characteristic of the variety and independent of the geographical origin of the fruit (*438*). No differences were observed in a qualitative study, in which filter-paper chromatography techniques were used, between the free amino acids in fresh single-strength orange juice and reconstituted, frozen, concentrated orange juice (*351*).

TABLE 3.—*Effect of heat and storage on some free amino acids in filtered California Valencia orange juice* [1]

Amino acid	Fresh juice	Loss of amino acids in —	
		Juice heated 12 minutes at 200° F.	Heated juice stored for 2 months at 100° F.
	Milligrams percent	*Percent*	*Percent*
γ-Aminobutyric acid	64	0	0
Aspartic acid	54	20	20
Serine	40	30	30
Glutamic acid	26	60	60
Alanine	26	60	60

[1] Rockland, L. B., and Underwood, J. C. Unpublished data.

TABLE 2.—*Cysteine and glutathione content of fresh and heat-treated citrus juices* (293) [1]

Juice	Cysteine			Reduced glutathione		
	Fresh	Heated [2]	Loss	Fresh	Heated	Loss
	Milligrams percent	*Milligrams percent*	*Percent*	*Milligrams percent*	*Milligrams percent*	*Percent*
Grapefruit	0.57	0.27	53	5.9	5.7	3
Lemon	.32	.28	13	2.8	2.1	25
Lime	.82			5.1		
Orange (Valencia)	.55	.41	25	7.8	5.6	28

[1] Roman numbers in parentheses here and in other table legends refer to Literature Cited, p. 81.
[2] In sealed, enamel-lined tin cans for 15 minutes at 212° F.

TABLE 4.—*Distribution of amino acids in late California Valencia oranges* (434)

Amino acid	Albedo	Flavedo	Segment membrane	Vesicles	Juice
Alanine	+	+	+	+	+
γ-Aminobutyric aci	+	+	+	+	+
Arginine	------	------	+	+	+
Asparagine	+	+	+	+	+
Aspartic acid	+	+	+	+	+
Glutamic acid	+	+	+	+	+
Glutamine	+	+	+	+	+
Leucine	+	------	------	------	------
Lysine	------	------	+	+	+
Methionine [1]	?	?	?	?	?
Phenylalanine	+	+	+	+	+
Proline	+	+	+	+	+
Serine	+	+	+	+	+
Threonine	------	+	+	+	+
Valine	+	+	+	+	+
Unknown	[1]+	+	+	------	+

[1] May be ornithine.

The distribution of free amino acids in the albedo, flavedo, segment membrane, vesicles, and juice of late California Valencia oranges is shown in table 4. Only minor differences were observed in the qualitative amino acid content of the tissues.

All the known nitrogenous constituents, other than the vitamins, that are found in various citrus juices are shown in table 5.

A protein fraction was isolated from the edible portion of the orange as early as 1925, and some of its general properties were briefly described (*400*). It was soluble in dilute (0.3 percent) alkali; was insoluble in water, neutral salts, and weak acids; was not coagulated by heat in neutral or alkaline solution; and had an isoelectric point at pH 4.7. Proteins have also been isolated from the edible portion of both California Valencia and Washington Navel oranges (*391*). The proteins from these two varieties appeared to be identical in respect to their total nitrogen, arginine, histidine, and lysine content. More recent qualitative studies have been conducted on the amino acids in the

TABLE 5.—*Nitrogenous constituents in citrus juices* [1]

Constituent	Orange		Tangerine	Grapefruit	Lemon	Lime	Dweet tangor	Mandarin			Lemon-orange hybrid
	Valencia	Washington Navel						Kara	Kinnow	Honey	
Alanine	(*351, 438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)
γ-Aminobutyric acid	(*351, 434, 438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)
Arginine	(*184, 351, 434, 438*)	(*438*)	(*438*)	(*438*)	0	0	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)
Asparagine	(*184, 351, 385, 434, 438*)	(*438*)	(*438*)	(*438*)	(*406, 438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)
Asparatic acid	(*184, 203, 351, 438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)
Betaine	(*184, p. 169*)	------	------	------	------	------	------	------	------	------	------
Choline	(*316, 426*)	------	------	------	------	------	------	------	------	------	------
Cysteine	(*203, 293*)	(*203, 293*)	------	(*293*)	(*293*)	(*293*)	------	------	------	------	------
Glutamic acid	(*351, 434, 438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)
Glutamine	(*385, 438*)	(*438*)	(*438*)	(*438*)	(*385*), 0	0	(*438*)	(*438*)	(*438*)	0	0
Glutathione	(*72, 203, 293*)	(*203, 293*)	------	(*293*)	(*293*)	(*293*)	------	------	------	------	------
Histidine	(*184, 203, 438*)	------	------	------	------	------	------	------	------	------	------
Leucine	(*351*)	------	------	------	------	------	------	------	------	------	------
Lysine	(*351, 434*)	------	------	------	------	------	------	------	------	------	------
Methionine	(*434*)	------	------	------	------	------	------	------	------	------	------
Phenylalanine	(*434*)	------	------	------	------	------	------	------	------	------	------
Proline	(*351, 434, 438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)
Putrescine	(*173*)	------	------	------	------	------	------	------	------	------	------
Serine	(*351, 434, 438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)	(*438*)
Stachydrin	(*316; 184, p. 169*)	------	------	(*125*)	------	------	------	------	------	------	------
Threonine	(*351, 438*)	------	------	------	------	------	------	------	------	------	------
Valine	(*351, 391*)	------	------	------	------	------	------	------	------	------	------

[1] Italic numbers in parentheses refer to literature citations; 0 indicates less than 5 mg. percent of the nitrogen constituent present.

protein obtained from both the peel and the edible portion of California Valencia oranges (*434*). Both the peel and the chromatophore protein fractions appeared to be qualitatively identical in terms of the constituent amino acids.

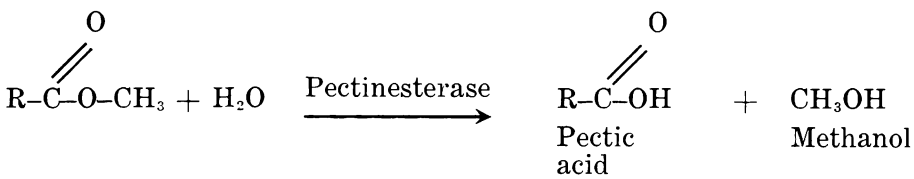
Enzymes

Enzymes are organic catalysts synthesized by living cells. They are among the most important constituents of living tissue, since it is through their action that the synthesis and alteration of other constituents and the energy metabolism essential to life are performed. Enzymes are considered protein in nature. Many require complex organic compounds called coenzymes, which are associated with the protein component and are equally essential for the activity of the enzyme. Thus, many of the water-soluble vitamins are known to be constituents of coenzymes, as, for example, thiamine (B_1), riboflavin (B_2), and nicotinic acid. The presence of these vitamins in living tissue suggests that related enzyme systems are also present in the tissue.

Enzymes have a number of properties that aid in their characterization. They are heat labile, and heating to boiling (212° F.) will inactivate most enzymes. Heat treatments of 158° to 176° for 2 to 5 minutes will bring about the inactivation of many enzymes. Certain enzymes are activated or stimulated by the presence of such cations as calcium or magnesium and by the presence of reversible oxidation-reduction systems, such as glutathione and methylene blue. Many enzymes are inactivated or irreversibly precipitated by heavy metal salts, such as lead and mercury. Most enzymes are reversible catalysts; that is, they can cause a reaction to go in either direction under suitable conditions, and therefore are theoretically capable of forming the same compounds they degrade. Probably the most characteristic property of enzymes is their specificity. One type is group specificity, in which the enzyme attacks only a certain chemical grouping, such as a carboxyl (COOH) group or an ester bond, without showing exclusive preference for the compound in which the bond occurs. Many enzymes exhibit absolute specificity, in which they are capable of effecting a chemical reaction in only one specific compound.

Enzymes are generally classified into broad groups according to the type of reaction they catalyze, such as hydrolytic and oxidation-reduction; and they are subdivided within these groups according to the type of molecule they attack and the type of bond in the molecule that is broken, such as *esterases, carbohydrases,* and *decarboxylases.*

Pectinesterase (pectin methylesterase, pectase) of citrus fruits has received more study than any other citrus enzyme (*219, 222, 261, 262, 366, 368, 410, 411, 415*). This enzyme catalyzes the hydrolysis of the methyl ester bond of the pectin molecule, forming pectic acid and methanol, as indicated in the following formula, where R represents the polygalacturonide chain of the pectin molecule:



Pectinesterase exhibits a maximum activity at about pH 7.0 to 7.5 in 0.15 molar sodium chloride, and demethylation of pectin in acid orange juice is accelerated by the divalent cations (*262*). Methods of pectinesterase assay have been devised and modified by numerous workers (*221, 258, 262*).These methods involve letting the enzyme act on pectin under standard conditions of substrate, pH, and cation concentration. The activity of the enzyme releases the esterified carboxyl groups in the pectin, and these are titrated with a standard base. The measure of enzyme activity is the amount of base used in maintaining a constant pH over a unit period of time. It is expressed in pectinesterase units (PEu) on the basis of milliequivalents of ester bond hydrolyzed per minute per unit of enzyme taken (milliliters or grams of preparation). It may also be expressed in pectin methylesterase units (PMU), which are calculated on the basis of milligrams of methoxyl split off per unit of enzyme preparation in 30 minutes. The relation of PEu to PMU is 1 to 960.

Pectinesterase has received a great deal of attention in the processing of citrus products, because it is believed to be one of the principal causes of instability known as "cloud loss" and "gelation" in unheated citrus juices and frozen concentrates. It is believed that when pectinesterase acts on pectic substances in orange-juice products, the resulting low-ester pectinic acids and pectic acid form insoluble complexes because of the acidity and cation content of the

juice. If the original pectin content is relatively low, the pectinic acids precipitate, carrying with them other suspended colloidal materials, which give orange juice its desirable turbid appearance. Such juice results in a clear, supernatant serum underlaid by an unsightly precipitate. If the original pectin concentration is somewhat higher, demethylation may result in the formation of a semirigid gel throughout the juice or concentrate.

Pectinesterase is found in all citrus fruits. It occurs in greatest concentration in the juice sacs and rag, with decreasing amounts in the flavedo, albedo, and juice (*205, 262, 366*). Many workers have studied methods of preventing or inhibiting cloud loss and gelation in citrus juices by heat inactivation of pectinesterase (*219, 367, 368, 410, 411, 415*).

Protopectinase is the enzyme believed responsible for the transformation of protopectin to soluble pectin in citrus and other fruits during the process of maturation and ripening. The presence of this enzyme is based on inductive reasoning and the fact that protopectin is altered in maturing fruit. The enzyme has never been demonstrated in vitro, and there is a possibility that it does not differ from pectin polygalacturonase.

Pectic acid depolymerase may occur in some citrus fruits. There is at least one report of a pectolytic enzyme in grapefruit, which was believed to be a pectic depolymerase (*338*).

Acetylesterase and other esterases besides pectinesterase (pectin methylesterase) have been reported in citrus by various workers. Acetylesterase is relatively nonspecific in that it hydrolyzes methyl, formyl, propyl, and butyl esters, as well as acetyl esters, and it may be identical with a similar enzyme reported in citrus that hydrolyzes methyl butyrate (*205*). Acetylesterase is found in oranges, grapefruit, and lemons; has a pH optimum between 5.5 and 6.5; and is found in all parts of the fruit, with the amount decreasing from the peel toward the center of the fruit. In contrast to pectinesterase the enzyme is little activated by cations.

Phosphatase is a widespread esterase, which rather nonspecifically hydrolyzes phosphate esters of many naturally occurring organic compounds, such as glycerophosphates, dipalmitylglycerophosphoric acid, ribonucleic acids, and phosphorylated starches, such as amylopectin. This enzyme has been extensively studied in citrus fruits (*14, 15*), and occurs in the peel and also in solution in orange, grapefruit, and lemon juices. It is readily inactivated by heating. For this reason it has been suggested that the determination of phosphatase activity in citrus juices might be employed as an index of pasteurization (*15*).

Proteinases are enzymes that hydrolyze proteins to smaller peptides or to free amino acids. A proteinase has been reported in citrus juices, especially lemon juice (*271*). However, very little research has been done on the proteinases of citrus, although the fact that free amino acids are found in citrus juices reflects their presence. *Peptidase*, a related enzyme capable of hydrolyzing peptides (resulting from proteinase activity) to free amino acids, has also been reported in citrus fruits (*204*).

Peroxidase is found in all citrus varieties and in all parts of the fruit, but it is especially active in the seedcoats of lemons (*91*).

Cytochrome oxidase, reported in citrus (*196*), is involved in an enzyme system that is probably responsible for the major part of oxygen uptake by the orange.

Decarboxylases are enzymes common to all living material, and nearly always are found to be substrate-specific proteins in conjunction with the compound cocarboxylase, which is a complex compound of vitamin B_1 (diphosphothiamine), or codecarboxylase, a complex compound of vitamin B_6. Decarboxylases are known that catalyze the decarboxylation of pyruvic acid and many of the amino acids. Glutamic acid decarboxylase has been reported in citrus fruits, and probably accounts for the finding in citrus juices of γ-aminobutyric acid, which would result from the action of this enzyme on glutamic acid. Probably other decarboxylases are also present in citrus fruits.

Phosphoribiosomerase has been reported in citrus.[4] This enzyme catalyzes the equilibrium between the aldose and ketose form of phosphoribose (a phosphorylated sugar).

Other enzymes are present in citrus fruits, which are yet to be identified. As enzymes are responsible for carrying on the chemical transformations essential for life, it is therefore logical to assume that living material has as wide an array of enzyme systems as it has constituents that are synthesized, broken down, or metabolized for energy.

Organic Acids

Citrus fruits are classed as acid fruits, because their soluble solids are composed chiefly of organic acids and sugars. The acidity of citrus juices is due primarily to their content of citric and malic acids (*151, 311, 392-394*). Trace amounts of tartaric, benzoic, and succinic acids (*41*), as well as oxalic (*287*) and formic acids (*142*), have also been reported. Citric acid accounts for the largest portion of the

[4] Unpublished observations by B. Axelrod, 1946.

organic acids in citrus fruits, and may make up as high as 60 percent of the total soluble constituents of the edible part of the lemon.

The acidity of citrus juices is ordinarily determined by titrating a known volume of juice with a standard solution of sodium hydroxide, phenolphthalein being used as the indicator (*10, p. 390*), and the results are expressed as anhydrous citric acid. With most citrus juices those substances that react with sodium hydroxide are mainly organic acids, so the titratable acidity of a juice will in general represent its free organic acid content.

The total organic acid constituents of orange, grapefruit, and lemon are essentially equal to the sum of the citric and malic acids, as shown in table 6.

TABLE 6.—*Analysis of the organic acids of California citrus fruits, expressed as the average number of grams per 100 gm.*

Fruit	Citric acid	Malic acid	Total
Orange (Valencia) (*392*):			
Immature	2.61	0.17	2.77
Mature	.94	.15	1.09
Grapefruit (*394*):			
Immature	2.64	.31	2.94
Mature	2.32	.27	2.57
Lemon (Eureka) (*393*):			
Immature	4.78	.34	5.12
Mature	6.83	.22	7.03

Although the titratable acidity of citrus juices represents the total amount of free acids present, it provides no information regarding their presence in other forms. For example, some of the organic acids may be in the form of salts, such as citrates, tartrates, malates, and lactates. Others may be in the form of esters. In orange juice it was found that the amount of salts of organic acids ("combined acids") was remarkably uniform during growth of the fruit, and any variations in acidity were due chiefly to changes in the concentration of free acids, particularly citric acid (*392*). A definite relationship was found to exist between the free acid- "combined acid" balance and the pH of the juices.

In other studies on Valencia oranges it was shown that the maximum amount of free acids developed early in the fruit and changed very little thereafter. However, the concentration of free acids in the juice decreased considerably during maturity, increasing fruit size diluting the juice; whereas there was a corresponding increase in the pH, owing chiefly to the decrease in concentration of citric acid (*397*). Changes in the free acids during maturation of grapefruit were similar to those of the orange (*394*). However, the free acids in lemons were found to increase and the pH to decrease with fruit maturation (*393*).

The titratable acidity of citrus juices offers no measure of their "active acidity," which depends on the ionic dissociation of acids in solution to yield free hydrogen ions (H+). The "active acidity," or hydrogen-ion concentration, is designated by the term pH, which mathematically is equivalent to the logarithm of the reciprocal of the hydrogen concentration in moles per liter. In common practice the pH may be determined by two methods—colorimetrically with suitable indicators and electrometrically with pH meters. The latter method is particularly useful for measuring the acidity of colored citrus juices.

Certain solutions possess the ability to resist a change in pH when a solution of different pH is added to them. This condition is termed buffer action of a solution. Citrus juices are highly buffered, as indicated by the fact that they show relatively little change in pH when hydrogen (H+) or hydroxyl (OH—) ions are added to them (*18, 396*). Mixtures of organic acids and their salts generally exhibit this behavior of buffer action. Citric and malic acids, plus their salts, form the main buffering system of citrus juices, which have their maximum buffering capacity on the acid side because of the high ratio of free acid to "combined acids" (salts). With such a buffer system citrus juices can be diluted greatly with water while showing only minor changes in pH. This is the reason the pH of citrus juices changes only slightly during the late stages of maturation and why juices of varying titratable acidity may have identical pH values.

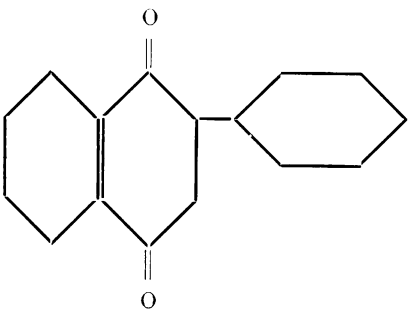
The titratable acidity of oranges and grapefruit plays an important part in determining the legal maturity of these fruits. Since the color of citrus fruits is not a dependable guide for ripeness, it is necessary to use some other measure of maturity. The ratio of soluble solids (as determined by the Brix hydrometer) to acidity has been established as a convenient index of maturity (*52, p. 30*). California requires a ratio of 8:1 for oranges and 7:1 for grapefruit before these fruits can be picked and shipped interstate (*53, p. 279; 111*). In Florida, fruit maturity is judged by the total soluble solids, a sliding scale of ratios of soluble solids to acid, and juice content, and must meet minimum color standards (*118, pp. 21-33*). In Texas, the ratio requirements for grapefruit are very similar to those in Florida and range from 6.5:1 to 7.2:1 (*432, pp. 131-134*). In California, lemons are purchased for processing on the basis of their citric acid content as deter-

mined by the titratable acidity rather than on a straight tonnage basis.

New analytical methods have been developed, including partition chromatography, columnar chromatography, and ion exchange, which should prove useful for characterizing in greater detail the organic acids and their various forms found in citrus juices (*249, pp. 114-131*).

Flavonoids

Chemically, flavonoids are organic compounds possessing the carbon framework of a flavone, or more broadly are C_6–C_3–C_6 compounds. The latter definition includes flavonols,



flavones, benzalcoumaranones, flavononols, flavanones, chalcones, anthocyanidins, dihydrochalcones, and catechins.

Flavonoids occur in the bark, twigs, leaves, flowers, and fruits of a large number of higher plants, and are frequently found combined with carbohydrate molecules as glycosides. Flavonoid compounds may compose as much as 10 percent of the dry weight of citrus fruits. The flavanone rhamnoglucosides hesperidin and naringin and their corresponding aglycones hesperetin and naringenin are the flavonoids associated with commercial varieties of citrus fruits (table 7).

Hesperidin was discovered in 1828 (*248*). It may be observed readily with the naked eye as an amorphous, white crystalline mass adhering to the segment membranes of an orange after exposure to freezing temperatures on the tree. It may also be seen at times as a sludge in cans of aged single-strength orange juice. Although hesperidin is insoluble in water and is tasteless, naringin (in grapefruit) is soluble in hot water and has an extremely bitter taste. The aglycone of naringin, naringenin, does not have a bitter flavor.

The function of flavonoids in citrus and other higher plants has not been established. It has been suggested that glucose in combination with flavonoid glycosides forms a soluble, easily hydrolyzable compound, and is thus temporarily inactivated until it is brought to that portion of the plant where the glucose is stored or utilized for metabolic processes (*141*). It has also been postulated that flavonoid compounds are the precursors or intermediary metabolites in the formation of a class of plant pigments known as anthocyanidins (*129*). Suggestions have been made that these compounds may act as light filters to regulate photosynthesis, or they may play an important part as components of oxidation-reduction systems (*63, 388*).

Flavonoids are of technological and economic interest to the citrus-processing industry (*170*). The flavor and general acceptability of grapefruit juice are strongly affected by the amounts of bitter principles, such as naringin, present in the product. Since the peel and pulp contain much greater amounts of the flavonoid compounds than the juice, great care must be exercised during juicing operations to minimize extraction of flavonoids from these nonedible portions of the fruit. In addition, the presence of excessive amounts of hesperidin in orange juice may at times result in the precipitation of this flavonoid in processing lines, and necessitate periodic, costly shutdowns of plant operations. It has been suggested (*149*) that flavonoids and other polyphenolic compounds may be of importance in the darkening and development of off-flavors in lemon and lime juices during storage at room temperatures.

Qualitative tests that have been employed for the detection of flavonoids and related polyphenols include the ferric chloride test (*152, 371*), the cyanidin reaction (*46, 371*), the borocitrate reaction (*476*), and the alkali test (*92, 254, 371*). Specific methods for the quantitative estimation of flavonoids in citrus fruits are not available. Several procedures have been suggested for the determination of flavonoids separated on filter-paper chromatograms (*97, 126-128, 337*). However, these procedures have not been applied to the determination of flavonoids in citrus products.

In spite of their nonspecificity the ferric chloride and the alkali reactions have been useful for estimation of total flavanones in citrus products. The distribution of total flavanones in mature California citrus fruits, calculated either as hesperidin or naringin, is shown in table 8. The rind, core, and segment membranes of citrus fruits contain from 75 to 90 percent of the total flavonoids. On a dry-weight basis these nonedible portions of the fruit may contain as much as 20 percent of flavonoid compounds.

The flavonoids in grapefruit and oranges have been studied more extensively than those in other citrus varieties. The naringin content of the rind of California grapefruit has been reported to decrease throughout the growing

TABLE 7.—*Flavonoids and flavonoid glycosides in citrus*

Common name of flavonoid	Chemical name or formula	Source			Literature citation
		Common name of fruit	Botanical species and variety	Part of fruit or tree	
Auranetin	3,6,7,8,4′-Pentamethoxyflavone	Myrtle-leaf orange	*Citrus aurantium* var. *myrtifolia* Ker-Gawl.		(*129*)
Aurantamarin	$C_{22}H_{71}O_{15}$	Bitter or sour orange	*C. aurantium* Linn		(*370, 427, 468*)
Citronetin	5,7-Dihydroxy,4′methoxyflavanone	Ponderosa, Wonder, or American Wonder lemon.	*C. limon* (Linn.) Burm. f.	Fruit peel	(*284, 488*)
Citronin	Citronetin-7-rhamnoglucoside	Lemon	*C. limon*	do	(*129, 488*)
Eriodictyol glucoside	5,7,3′,4′-Tetrahydroxyflavanone-glucoside.	Lemon	*C. limon*		(*468*)
		Sweet orange	*C. sinensis* (Linn.) Osbeck (*C. aurantium* var. *sinensis* Linn.).		(*468*)
Hesperetin	5,7,4′-Trihydroxy,3′methoxyflavanone	Myrtle-leaf orange	*C. aurantium* var. *myrtifolia*		(*339, 495*)
Hesperidin	Hesperetin-7-rhamnoglucoside	Sweet orange	*C. sinensis*	Blossom petals	(*157*)
			C. kotokan Hayata	Fruit	(*191*)
		Lemon	*C. limon*	Leaves, fruit	(*260, 468*)
		Citron	*C. medica* Linn		(*468*)
		Sweet orange	*C. sinensis*	Juice, leaves, twigs, bark	(*129, 178, 248*)
			C. tankan Hayata	Fruit	(*437*)
Hesperidin chalcone		Lemon	*C. limon*		(*468*)
Naringenin	5,7,4′-Trihydroxyflavanone	Shaddock or pummelo	*C. grandis* (Linn.) Osbeck	Fruit, flowers	(*8, 226*)
Naringin (isohesperidin)	Naringenin-7-rhamnoglucoside	Sour orange	*C. aurantium*		(*158, 370, 468*)
		Shaddock or pummelo	*C. grandis*		(*8, 9, 129, 468, 475*)
		Grapefruit	*C. paradisi* Macf.	Fruit juice, peel	(*16, 475*)
		Trifoliate orange	*Poncirus trifoliata* (Linn.) Raf.	Fruit, leaves	(*155*)
Neohesperidin	Hesperetin-7-glucorutinoside	Trifoliate orange	*P. trifoliata*	Unripe fruit	(*226, 282, 427*)
			C. fusca Lour.	Fruit	(*191*)
Nobiletin	5,6,7,8,3′,4′-Hexamethoxyflavone	Mandarin orange	*C. reticulata* Blanco		(*239, 437*)
			C. tankan	Fruit	(*437*)
Ponciridin		Trifoliate orange	*P. trifoliata*		(*468*)
Poncirin	5,7-Dihydroxy-4′-methoxyflavanone	do	*P. trifoliata*	Fruit, flowers	(*155, 156*)
Ponkanetin	5,6,7,8,4′-Pentamethoxyflavone	Chinese honey orange	*C. poonensis* Hort. ex Tanaka	Fruit	(*149, 198*)
Rhoifolin	5,7,4′-Trihydroxyflavone-7-rhamnoglucoside.	Sour orange	*C. aurantium*	Ripe fruit	(*158*)
		Trifoliate orange	*P. trifoliata*	Leaves	(*156*)
Rutin	3,5,7,3′,4′-Pentahydroxyflavone-3-rhamnoglucoside.	Satsumelo	*C. paradisi* × *C. nobilis* Lour.	Fruit rind	(*242*)
Tangeretin	3,5,6,7,4′-Pentamethoxyflavone	Tangerine	*C. reticulata*	Fruit rind, oil	(*468*)
		Dancy tangerine	*C. tangerina* Hort. ex Tanaka		(*139, 313*)
Tricin	5,7,4′-Trihydroxy-3′,5′-dimethoxyflavone.	King mandarin	*C. nobilis*		(*139*)

TABLE 8.—*Distribution of flavanones in citrus fruits* (91)

Fruit	Juice (grams per 100 ml.)			Tissue (percent, wet basis)				
	Fresh centrifuged	Sediment	Total	Juice sacs	Section membrane	Albedo	Flavedo	Core
Grapefruit [1]	0.038	0.003	0.041	0.140	1.250	2.100	0.600	2.600
Lemon [2]	.046	.008	.054	.600	1.900	3.000	2.500	----------
Orange [2]	.080	.038	.118	----------	1.500	1.600	1.000	4.500
Tangerine [2]	.065	----------	----------	----------	.500	[3]1.700		[4]1.570

[1] Calculated as naringin.
[2] Calculated as hesperidin; eriodictyol glucoside may be present and would be included in the calculation as hesperidin.
[3] Determination made on whole peel.
[4] Fibrovascular and adhering tissue, as tangerines have no core.

season (*153*). The locality in which the grapefruit is grown has a marked effect on the rate of change in naringin content during storage of the fruit at low temperature.

In a study conducted in Texas during the 1948 harvest a marked change in the naringin content of grapefruit occurred within 1 month (*282*). Decreases in naringin content of from 45 to 66 percent were observed in the juices and various tissues. Juice samples containing more than 0.07 percent of naringin had an immature, bitter taste, whereas samples containing less than 0.05 percent had a superior flavor. No change in naringin content was observed during commercial processing.

The naringin content of the peel and pulp of California grapefruit was found to be considerably higher than that of Florida grapefruit. The values reported were 0.90 and 0.40 percent in the peel and 0.15 and 0.10 percent in the pulp of the California and Florida fruit, respectively (*225*).

A comprehensive study of the naringin content of the shaddock and 5 Florida grapefruit varieties has been reported (*226*). The quantity of naringin in these fruits was found to remain constant once the fruit had grown to 2 inches in equatorial diameter. Thereafter, as the fruit grew larger, the naringin content on a percentage basis became lower. The naringin content varied from 6.2 to 1.3 gm. per fruit. On a percent-by-weight basis Ruby Red grapefruit contained the highest percentage of naringin. Almost 90 percent of the naringin was found in the albedo, rag, and pulp. The naringin content of the juice decreased or increased at the expense of the pulp and rag, the albedo and flavedo accounting for a uniform percentage of the total. The percentage by volume of naringin in the juice, which could not be satisfactorily correlated with maturity, varied between 0.02 and 0.03 percent throughout the season.

A similar study by the same workers (*170*) on the estimation of the total flavanones, calculated as hesperidin, in four varieties of Florida oranges gave essentially the same results as their grapefruit studies, except that the total flavonoids in the nonedible portion accounted for only 75 to 80 percent of the total and the hesperidin content of the juice varied between 0.015 to 0.025 percent.

A value of 0.046 percent of hesperidin has been reported for California single-strength filtered lemon juice (*260*).

Bitter Principles

Washington Navel oranges as grown in California are seldom used for the manufacture of canned juices or concentrates, because when the extracted juice is heated or allowed to stand, a bitter or astringent flavor usually develops, rendering it unpalatable. The intensity of this bitterness is dependent on the maturity of the fruit, being most pronounced in juices from early-season fruit, and it may vary from season to season. Bitterness may also be found in the juice of immature Valencia oranges, but it always disappears before this variety reaches commercial maturity.

The exact chemical nature of the bitter principles and the mechanism of their formation are still obscure in spite of the large amount of work carried on by a number of workers (*59-61, 107-110, 130, 218, 240, 241, 377*). It is believed that unknown precursors are present in the albedo, center core, and segment membranes of the fruit in a nonbitter, water-soluble form. When these tissues are ruptured during the extraction process, nonbitter precursors are dissolved into the acid juice, where they are converted by some means yet unknown to the bitter compounds limonin and/or isolimonin. As little as 1 part of limonin in 100,000 parts of water will give a very bitter taste. Limonin,

not to be confused with the terpene of peel oil, limonene, and isolimonin have been isolated and partially characterized, and some of their chemical and physical properties determined.

Limonin has been isolated as a white crystalline substance having a melting point of 555° to 557° F. and with the empirical formula $C_{26}H_{30}O_8$. Limonin and or isolimonin are soluble in alcohol, acetone, and benzene, but relatively insoluble in petroleum ether and extremely insoluble in water. Limonin forms tasteless salts with alkaline earth metals, but below pH 6 or 7 the salts revert to the bitter lactone form of the compound. The water-soluble precursor might be either a glycoside, which hydrolyzes in the presence of air and juice acids to release the bitter compound, or a tasteless, water-soluble free acid, which in the presence of air and juice acids lactonizes to form the bitter compound (*176, 177*).

Further work on the chemistry of the bitter principles in Washington Navel oranges has indicated that limonin and or isolimonin of the juice may be identical. A related compound, nomilin, found only in the seeds of oranges and lemons, has also been reported (*107-110*). Nomilin has the empirical formula $C_{28}H_{34}O_9$, and both limonin and nomilin are believed to contain 2 lactone rings. It has been proposed that limonin occurs in situ as a water-soluble free acid which, when extracted into Washington Navel juice, forms the bitter di-lactone limonin. In addition to the 2 lactone rings, degradation studies indicate that limonin contains in its chemical structure 1 carbonyl group and 3 cyclic ether rings. It is believed that the bitterness of these compounds, particularly limonin, is associated primarily with one of the lactone rings. The addition of a base to solutions of limonin causes the opening of the lactone ring and the formation of a nonbitter salt.

Another bitter principle has been reported that is believed to occur naturally in the peel as well as in the seeds of Navel oranges grown in Australia (*61*). This compound has been named limonexic acid, and has the empirical formula $C_{25}H_{30}O_{10}$. Like the other bitter compounds, limonexic acid possesses at least one lactone ring, which opens on treatment with a base to form a nonbitter salt. The finding of this new bitter principle may explain some of the conflicting results obtained by workers who have attempted to debitter Washington Navel orange juice.

Numerous attempts have been made to prevent the development of or to remove bitterness from Washington Navel orange juice in order to make processing feasible from season to season. In one of the first methods the combination of a special type of burr was used for reaming the juice to prevent excessive extraction of rag and pulp, in conjunction with a process of increasing the hydrogen-ion concentration of the juice to pH 3.8-4.0 by the addition of carbonate salts to minimize formation of the bitter lactone (*177, 179*). The difficulty in this method lies in the fact that it is not easy to prevent complete bitterness formation without increasing the pH beyond the point where juice flavor is affected. Another attempt involved the use of pectic enzymes. The objective was to use their action on natural pectic substances in the juice and thus coagulate the dispersed colloids that precipitate and, incidentally, to remove the limonin in suspension (*256*).

In a third method (*256*) activated carbons completely removed the bitter principle or principles and their precursors. However, the method presents technical difficulties, the chief of which are the tendency of carbon "fines" to be suspended in the juice and a partial loss of vitamin C.

None of these methods are considered successful or feasible for commercial application at the present time.

Besides seasonal variations in bitterness and variation of bitterness with maturity, it has been shown that for a given season or at a given stage of maturity bitterness varies greatly with the type of rootstock on which fruit is grown (*272*). Thus, Washington Navel oranges grown on rough lemon rootstock never lose the bitter principles with maturity, whereas Washington Navels grown on grapefruit rootstock always lose the bitter principles upon reaching commercial maturity. Washington Navels grown on other rootstock are variable in the occurrence and intensity of the bitter principles and the point of maturity when bitterness disappears, as illustrated below.

Rootstock of—	*Time of disappearance of bitterness*
Grapefruit	Upon commercial maturation; 8:1 ratio.
Trifoliate orange	Few weeks after commercial maturation.
Sweet orange	Do.
Sour orange	Late in the season.
Washington Navel cutting.	Do.
Rough lemon	Never.

It is seen that in studying loss of bitterness in Washington Navel oranges with maturation it is necessary to know the type of rootstock on which the fruit is grown. It is also seen to be theoretically possible to raise Washington Navel fruit that will not be bitter after maturation by proper rootstock selection or by adjusting the processing season to the type of rootstock from which the fruit is obtained.

In California most Washington Navel oranges are grown on rootstocks that cannot be relied on to yield nonbitter juice when the fruit is commercially mature. It is also impracticable to segregate the fruit for processing according to the rootstock from which it is picked. Therefore, it is seldom safe to process Washington Navel oranges for juice, and in "bitter" years the entire crop must be sold as fresh fruit or processed for byproducts.

If it should become more desirable or necessary to process Washington Navel orange juice, the most satisfactory solution of the problem of bitterness appears to lie in a gradual changeover to nonbitter rootstocks.

Volatile Flavoring Constituents

The volatile constituents of citrus juice are defined as those materials that can be removed from the juice by distillation methods. They will include a large amount of water, volatile oils that are steam distilled along with the water, and other constituents that boil at temperatures lower than water or are removed as azeotropic mixtures with water.

If the volatile constituents are removed from the juice by distillation at atmospheric pressures, their composition is considerably altered in the process. If they are removed by distillation at reduced pressures and correspondingly lower temperatures, the recovered fraction resembles more closely the aroma of the original juice; the lower the temperatures of distillation, the more closely the volatiles resemble the original aroma. Some of the volatile constituents are gaseous in their normal state, and elaborate methods must be employed to trap them.

A citrus juice from which a portion of the water has been removed by distillation shows a definite change in flavor, and it was early recognized that the aroma of orange juice was associated with the volatile fraction (*142*). The flavor of a concentrated orange juice that has been restored to its original consistency by the addition of pure water tastes insipid and is lacking in orange character (*354*). It is now generally recognized that the flavor and aroma of fresh orange, as well as certain off-flavors of the processed juice, are associated with the volatile fractions (*36, 40, 171*). Grapefruit juice from which a portion of the water has been removed tastes only sweet and sour (*234*). Examination of other citrus juices for the relationship between volatile materials and flavor and aroma has not been reported, but it can be expected that they will show the same relationship as has been reported for orange and grapefruit juices. No systematic work has been recorded in the literature as to what fraction of water must be removed from the juice to remove all of the volatile flavor.

The isolated volatile fraction consists of constituents that are soluble and those that are insoluble in water. Whereas some of the aroma resides in the water-soluble fraction (*142, 234, 301*), most of the flavor and aroma of citrus juices are found in the volatile, sparingly soluble oil fractions (*233, 234, 301, 354*). Some methods of commercial extraction of the juice from the fruit result in the incorporation of some peel oil into the juice. However, the juice itself contains some oil present in the juice sacs. Experiments with carefully peeled and washed fruit, followed by analysis of the juice for oil content, showed appreciable amounts of oil (*36, 40, 301, 354*). For oranges, the juice-sac oil has been estimated at 0.0006 to 0.006 percent (*301, 354*). Globules of oil have been demonstrated in the juice sacs of various citrus fruits (*90*). It has also been claimed that these globules do not contain oil, only starch and protein, but no test had been made for the presence of essential oils (*231*).

Methods for the determination of amounts of volatile oils in citrus juices have been published (*19, 47, 383*), and a review of various types of apparatus used for this purpose is available (*80*). The official method of the United States Department of Agriculture is given in the Standards for Grades of Frozen Concentrated Orange Juice (*441*). The amounts of volatile oil present in commercially extracted grapefruit and orange juices have been reported to vary from 0.008 to 0.014 percent and 0.016 to 0.075 percent, respectively (*301, 354, 383*).

Analyses of the composition of the different volatile constituents in citrus juices are difficult to attain. Not only are these materials present in very small amounts, as previously indicated, but they consist of complex mixtures of closely related substances sensitive to heat and light.

The gaseous substances in variously extracted orange and grapefruit juices have also been investigated (*347*). The juices contained from 22.3 to 41.7 ml. of carbon dioxide, 2.22 to 4.02 ml. of oxygen, and 9.7 to 13.9 ml. of nitrogen per liter of juice. The ratio of oxygen to nitrogen in these samples is significantly different from that of air.

For the most part the analysis of the other volatile constituents of citrus juices is incomplete, qualitative in nature, and sometimes based on inconclusive evidence. The acetaldehyde content of fresh lemon pulp has been found to vary between 0 and 1.3 mg. per 100 gm. of pulp (*289*). Isoamyl alcohol has been identified in lemon juice by a ferric alum test,

and isovaleric acid by odor (*123*). Orange juice has been more extensively investigated than other citrus juices, particularly as regards changes in the composition of the volatile fractions on heating and storage. One of the earliest researches in this connection was that of Hall and Wilson (*142*). Unfortunately in obtaining the volatile material the whole fruit was crushed, and the oil layers from successive distillations were systematically discarded until the volume of distillate had been reduced to 0.1 percent of the original. The oil that was present in the juice sacs and that contributed greatly to the flavor was thus discarded with the peel oil. The following constituents were reported to be present: Acetone, acetaldehyde, ethyl alcohol, formic acid, citronellal, esters of capryllic, acetic, and formic acids, isoamyl alcohol, phenylethyl alcohol, possibly geraniol, possibly terpineol, and a $C_{10}H_{18}O$ alcohol similar to linalool.

More recently it has been found that a low-temperature distillation or a petroleum ether extraction removed all the odor and flavor from canned orange juice (*171*). In this work a precipitate of carbonyl compounds was obtained from the volatiles with 2,4-dinitrophenylhydrazine, and no change in odor was detected, although the odor was destroyed by either potassium permanganate or bromine. No change in odor was noticed when the mixture was distilled from an alkaline solution, indicating that organic acids were not concerned in the odor. Unsaturated hydrocarbons and alcohols were concluded to be responsible for the off-odors and off-flavors associated with canned orange juice.

In further work with canned orange juice and limonene in citrate-buffered model systems, the infrared spectra of a number of variously stored samples have been determined (*36*). From these data and theoretical considerations of the reaction of limonene in an acidic aqueous medium, it was concluded that 1,4-cineol, terpineol, and terpinolene were formed and esters were hydrolyzed by heat and storage conditions; thus off-flavors were produced.

Hydrogen sulfide has been reported in green citrus fruits and juices (*21, 235*). Furfural has been detected in orange juice stored in the presence of oxygen (*307*), and the acetaldehyde and alcohol content of orange juice as affected by the season has been determined (*436*).

A comprehensive study has been made on the volatile constituents in grapefruit juice (*233, 234*). Newly developed chromatographic techniques were used, which minimized any chemical changes during analysis. Table 9 gives the results of this work.

TABLE 9.—*Volatile constituents of grapefruit juice, expressed in milligrams per kilogram of juice*

Constituent	Fresh juice	Freshly canned juice	Stored 4 years at room temperature
WATER-SOLUBLE CONSTITUENTS			
Acetaldehyde	1.45	0.33	0.6
Acetic acid	0	1.9	23.3
Acetone	0	0	.1
Acid A ($C_6H_8O_2$)	0	4.8	2.9
Acid B ($C_6H_8O_2$)	0	1.9	1.6
Acid C	0	[1]	0
Ethyl alcohol	400.0	400.0	460.0
Furfural	0	[1]	8.2
Hydrogen sulfide	[1]	0	[1]
Methyl alcohol	.2	.2	23.0
WATER-INSOLUBLE CONSTITUENTS			
Total oil	20.92	26.00	27.59
Limonene	15.71	17.70	11.17
α-Pinene	[1]	[1]	[1]
α-Caryophyllene	.10	.10	.12
β-Caryophyllene	1.40	1.40	.87
$C_{15}H_{24}$	.11	.11	.14
$C_{15}H_{28}$	[1]	[1]	0
Low-boiling hydrocarbons	[1]	[1]	[1]
N-Methyl methyl anthranilate	[1]	[1]	0
$C_{13}H_{15}N$	[1]	[1]	0
Caryophyllene oxide	.80	.80	.27
Citral	[2] 1	[2] 1	[2] 1
Carvone	[2] 1	[2] 1	[2] 1
$C_{15}H_{26}O$	.19	.23	.54
Linalool	.16	.23	.08
$C_{15}H_{22}O$	.45	.42	.64
Carveol	.30	.30	.27
α-Terpineol	.03	.88	2.02
3-Hexen-1-ol	.12	0	0
Geraniol	[2] .05	[2] .05	0
Linalool monoxide	.37	2.03	8.95
$C_{12}H_{20}O_2$	.20	.20	.20
Polyoxygenated compounds	.40	.86	.97
Oxides	.32	.32	.32

[1] Trace.
[2] Approximate.

In general, the volatile material consists of water-soluble compounds, which would not be expected to contribute to flavor; terpene hydrocarbons, which have a turpentine-like odor; and nonhydrocarbons, mostly terpene derivatives, which produce the characteristic odor and flavor. The objectionable character of canned and stored grapefruit juice arises from the decomposition of the terpene hydrocarbon fraction to α-terpineol and linalool monoxide, aided perhaps by the formation of methanol, acetic acid, and furfural from sources within the juice other than the terpene hydrocarbons.

Pigments

The color of citrus fruits is due to a class of compounds called pigments, which are located in various portions of the fruit, but generally are found in the cells of the outer peel (flavedo) and in the juice sacs. These pigments are not uniformly distributed throughout the cells, but are concentrated in minute structures called plastids, or chromatophores. The size and shape of these plastids appear to be characteristic of the species from which they are obtained (*277*). Not all the coloring matter is in the plastids. For example, the characteristic color of the peel of mature limes is found in the cell sap (*149*), and the pigments of orange and tangerine peel are in the cell walls (*489, 490*). In some grapefruit and in the blood orange the color has been reported to be in the cell sap.

The pigments of Foster and Marsh pink grapefruit are lycopene and β-carotene (*280*), the latter predominating in the Marsh pink grapefruit. This explains why the Foster is a true pink and the Marsh a salmon pink. Lycopene is also present in the Indian Red pummelo (*279*). Anthocyanin occurs in the juice sacs of the blood orange (*278*).

The color of green fruit is due to the presence of chlorophylls *a* and *b*. As they decrease carotenoids increase and continue to increase after the chlorophylls have disappeared (*291*). Although all the pigments in citrus fruits have not been identified, the following have been reported in the peel and juice of oranges: Citroxanthin (*215*); α-, β-, and ζ-carotene (*83, 275, 308*); cryptoxanthin (*83, 291, 493*); zeaxanthin (*83, 308, 493*); lutein (*83, 308, 493*); violaxanthin (*493*); citraurin (*493, 494*); phytofluene (*83, 308*); hydroxy-α-carotene (tentatively identified) (*83*); flavoxanthin (tentatively identified) (*308*); an unidentified acidic red pigment (*423*); and phytoene (*349*). The color of lemons is due principally to two groups of pigments, the chlorophylls and carotenoids (*290*), and limes owe their color to carotenoids and phlobatannin (*149, 290*). Tangeretin (*313*), β-carotene, lutein, violaxanthin, and cryptoxanthin (*489*) have been reported in the tangerine, and β-carotene (*491*) and cryptoxanthin (*492*) in the mandarin.

Methods for the isolation and analysis of pigments present in the various parts of citrus fruits are long and complicated. Usually they consist of drying or filtration; extraction with a suitable solvent; removal of the solvent; destruction or removal of extraneous material; saponification of the residue and separation of of the pigments by solubility, chromatography, counter-current extraction, or combinations of these; and finally, measurement in a colorimetric apparatus. A number of simple and complex methods have been described in the literature for the isolation and identification of chlorophyll and carotenoid pigments in citrus products (*83, 330, 429, 490-494*).

The amounts of pigments found in citrus fruits vary with the species, stage of maturity, seasonal variations, and region in which they are grown (*5*). In an analysis of 164 samples of Florida and California orange juices, the carotene content varied from 0.32 to 1.65 mg. per liter of juice (*429*).

Whole fresh oranges contain around 18 mg. of carotenoids per kilogram (*493*), although amounts several times this figure have been found; and various quantities have been reported to be present in the tangerine (*349, 489, 492*).

Carotenoid pigments are important from the standpoint of nutrition, because some have vitamin activity.

Sugars

The sweetness of citrus fruits is due to the presence of glucose, fructose, and sucrose. Total sugars may vary from less than 1 percent in certain limes to nearly 15 percent in some oranges. Besides the wide characteristic differences among the various kinds of citrus fruits, there are a host of other factors, such as variety, climate, rootstock, available plant foods, and maturity, that influence the sugar content. In addition, location of the fruit on the tree influences sugar content, those receiving the most sunshine having the highest sugar concentration. In general, juice from the stylar half of the fruit is sweeter than that from the stem half, and neighboring segments within a single fruit have been reported as differing as much as 2.7 percent in soluble solids.

Other factors remaining constant, probably the most important variable governing sugar content is maturity, especially with the sweeter kinds of citrus. In these the acid content declines slightly during maturation, but the sugar content increases (*144, 146, 148*). This fact is used in judging maturity, according to State and Federal laws and regulations. In the sweeter fruit juices, such as those from oranges, tangerines, and grapefruit, the soluble solids consist mainly of sugars, but in lemon juice and especially in lime juice the soluble solids are chiefly citric acid.

Citrus fruits contain both reducing (fructose and glucose) and nonreducing (sucrose) sugars. In oranges at maturity these types of sugars are present in about equal amounts, but in the less sweet fruits, such as limes and lemons, reducing sugars predominate. In mature tangerines the reverse is true, the nonreducing sugars

exceeding the reducing sugars in amount (*362*). Table 10 gives the sugar content for several kinds of citrus juices.

TABLE 10.—*Approximate sugar content of some citrus juices*

Fruit variety	Locality grown	Reducing sugars	Nonreducing sugars	Total sugars
		Percent	*Percent*	*Percent*
Grapefruit:				
Duncan (*144*)	Florida	3.0–5.1	2.4–4.0	5.0–8.3
Marsh (*144*)	do	2.3–4.8	2.6–3.1	5.1–7.8
Lemon:				
Eureka (*20*)	California	.78–2.6	.03–.63	.81–3.2
Meyer (*407*)[1]	Florida	3.22	.48	3.70
Villafranca (*407*).[1]	do	1.29	.05	1.34
Lime:				
Key (*407*)[1]	do	.64	.12	.76
Tahiti (*407*)[1]	do	1.29	.10	1.39
Orange:				
Hamlin (*148*)	do	2.6–3.0	2.0–3.9	4.6–6.7
Homosassa (*148*).	do	2.8–3.5	1.7–2.7	4.5–6.0
Parson Brown (*148*).	do	3.4–4.8	2.6–4.4	6.8–8.7
Pineapple (*148*)	do	2.5–3.9	1.5–3.1	3.9–6.4
Valencia (*148*)	do	3.2–5.0	2.3–5.2	5.4–10.3
Washington Navel (*390*).	California	4.3–5.8	.....	7.3–10.5

[1] Recalculated on a juice basis from the original data.

The occurrence of these different sugars is based on chromatographic, chemical (*472*), and polarimetric (*86*) evidence, at least as far as oranges, grapefruit, and lemons are concerned. There are data (*473*) to show that the edible portion of the lemon contains 1.40 percent of glucose, 1.35 percent of fructose, and 0.41 percent of sucrose; whereas the juice contains 0.52 percent of glucose, 0.92 percent of fructose, and 0.18 percent of sucrose.

The proportions of sucrose, fructose, and glucose have been determined in a few samples of orange juice. These results are summarized in table 11.

The fact that glucose and fructose are present in about the same amounts suggests that sucrose has been inverted. However, it is not known whether this relationship holds for other citrus fruits or, indeed, for all oranges.

When orange juice and presumably juice from other citrus fruits are pasteurized and canned, inversion of sucrose occurs in storage. In one such case (*459*) it was found that in 9 months there was an 81-percent loss in sucrose, with a corresponding increase of 69.8 percent in reducing sugars.

Sugars also occur in the albedo, or white portion, and in the flavedo, or outer colored portion, of the peel, as well as in the rag. On a fresh-weight basis Poore (*335*) reported 8.68 percent of sugars in California grapefruit peel and rag combined. In Florida grapefruit peel he found 6.35 percent of sugars and in the rag 6.30 percent. These sugars are free, and these values do not include the higher carbohydrates present, such as cellulose, starch, hemicellulose, pentosans, and pectin, which give sugars and sugar derivatives on hydrolysis. Haas and Klotz (*137*) have shown that the concentration of sugars is higher at the stem end of the fruit than at the stylar end—just the reverse of the sugar-concentration gradient in the juice. Table 12 gives the sugar content of California grapefruit, lemon, and orange rinds.

TABLE 11.—*Sucrose, fructose, and glucose contents of Valencia orange juice, based on the total sugars present*

Origin	Year	Sucrose	Fructose	Glucose
		Percent	*Percent*	*Percent*
California (*260*)	1946	49.4	25.3	25.3
	1947	59.5	18.0	22.5
Florida (*86*)	1944	50.5	25.8	23.7

TABLE 12.—*Sugars in the rinds of California grapefruit* (153), *lemons* (20), *and oranges* (154)[1]

Fruit	Reducing sugars, expressed as glucose	Sucrose, expressed as invert sugar	Total sugars
	Percent	*Percent*	*Percent*
Marsh grapefruit	14.2–26.2	7.6–16.3	21.8–42.5
Lemon (mature)	20.0	[2]1.6	21.6
Valencia orange	15.4–27.9	6.1–13.4	21.5–41.3
Washington Navel orange	30.4–34.9	4.8–6.6	35.2–41.5

[1] Data are condensed and are expressed on a dry basis.
[2] Nonreducing sugars.

References are given in the literature to the occurrence in citrus peel of pentoses, which are 5-carbon sugars, whereas glucose and fructose have 6 carbons. Usually these references are to substances that can give pentoses on hydrolysis, or hydrolysis and decarboxylation, rather than the free, preformed pentoses. Thus, any pentosans present could be hydrolyzed to pentoses, or a pentose could readily be derived from pectin by hydrolysis to galacturonic acid with subsequent decarboxylation.

Glycosides, such as naringin in grapefruit and hesperidin in oranges, are constituents of juice, peel, and rag and give sugars on hydrolysis.

Lipids

This term ordinarily means those substances that are insoluble in water but are soluble in fat solvents, such as diethyl ether, petroleum ether, chloroform, and benzene. They are not volatile in steam, which is one distinction from essential oils, such as citrus-peel oils. Essential oils have quite different chemical structures from lipids, and are usually strongly odoriferous.

There are several classes of lipids, and they are usually grouped under three general headings:

(1) Simple lipids, including the neutral fats, which are esters of glycerol (an alcohol) and fatty acids. Citrus-seed oil is an example.

(2) Compound lipids, which include compounds of fatty acids with an alcohol (sometimes glycerol), but containing other groups in addition to the alcohol. In this class are phosphatides, such as lecithins and cephalins, both constituents of orange-juice lipids.

(3) Derived lipids, which may be listed under several subheadings. Among these are free fatty acids, alcohols (straight-chain and sterols), and hydrocarbons, including certain of the carotenoids. Examples of all of these subclasses are found in citrus-juice, peel, and pulp lipids.

Citrus-seed oils contain, like most vegetable-seed oils, a small amount (less than 1 percent) of unsaponifiable matter. In addition, they contain a bitter principle, probably limonin, which can be removed by alkali refining, and the closely related bitter substance nomilin (*107*), which somewhat limits the usefulness of the crude oil in food products.

Physical and chemical constants for a few citrus-seed oils are given in table 13. It should be understood that these values are based on single samples of oil and therefore are not necessarily typical. These data indicate that citrus-seed oils are of the semidrying type and that they are comparable to cottonseed and many other seed oils in constitution.

In addition to these seed oils, which are simple lipids, there are deposits of lipids in other parts of the fruits. These are mixtures of compound and derived lipids, and they occur as certain cell inclusions, such as plastids, and possibly in association with the intercellular membranes. Thus when juice is extracted, these compound and derived lipids occur in suspension and are associated with cellular debris. For this reason direct extraction of lipids with solvents is impracticable because of troublesome emulsions and the collection of suspended matter at the interface.

A more effective method of lipid extraction for the purpose of study is to separate the suspended matter by centrifugation or, better yet, filtration with a filter aid, followed by subsequent extraction of this material with acetone.

TABLE 13.—*Physical and chemical values for citrus-seed oils*

Item	Florida grapefruit		California orange hydraulic-press oil (*447*)	Florida tangerine solvent-extracted oil (*422*)	West Indian lime oil (*103*)	Lemon oil (usual range) (*104*)
	Expeller oil (*202*)	Expeller oil (*318*)				
Specific gravity (25° C.)	0.9170	0.9197	0.9153	0.9165	----	0.916–0.919
Refractive index (*nD*, 25° C.)	1.4700	1.4698	1.4686	1.4702	[1]1.4676	[1]1.463–1.466
Acetyl value	7.7	2.4	----	8.2	----	----
Acid value	2.5	.95	----	4.31	----	----
Saponification value	194.1	193.0	197.5	193.55	195.2	188.0–196.0
Unsaponifiable matter (percent)	.7	.48	.95	.54	.6	.4–.8
Iodine value	[2]106.3	[2]100.9	[3]101.7	[3]107.3	111.1	103.0–109.0
Thiocyanogen value	----	----	----	66.37	----	----
Constituent fatty acids (percent):[4]						
Arachidic	----	----	.9	1.1	.5	----
Hydroxy	----	----	----	2.9	----	----
Lignoceric	.1	----	----	----	----	----
Linoleic	51.0	----	36.5	46.6	39.3	----
Linolenic	----	----	.6	2.1	13.1	----
Myristic	----	----	----	----	.3	----
Oleic	20.5	----	36.6	22.5	11.1	----
Palmitic	20.1	----	20.7	19.6	26.1	----
Stearic	7.6	----	4.7	5.2	9.6	----

[1] At 40°C.
[2] Hanus method.
[3] Wijs method.
[4] The fatty acid data for grapefruit are expressed as percent acid glycerides of total glycerides, for oranges and limes as percent acids of total mixed acids, and for tangerines as percent methyl esters of acids of total methyl esters. Numerically, the expression for tangerine oil is practically equivalent to the percent acid glycerides of total glycerides.

Evaporation of this solvent and extraction of the residue with petroleum ether serve to eliminate water extracted by the acetone. When the petroleum ether is evaporated under vacuum, the lipids are obtained as a viscous liquid, which in oranges is deep red in color but which would undoubtedly differ in hue and intensity when extracted from other citrus fruits. This method of lipid recovery has been used as the basis of an analytical method of lipid determination (*421*). In amount the yield from juices usually falls within the range of 0.05 to 0.1 percent, depending somewhat on the type of juice extractor employed and of course on the particular fruit sample.

None of the citrus-juice lipids have been studied in much detail except those from oranges. Even in this case little is known about the so-called resin acids, one of the constituents found in the lipid fraction. Information about the unsaponifiable fraction is far from complete although some work on the carotenoid pigments has been reported (*83*). Table 14 gives the probable composition of two samples of orange-juice lipids as calculated from analytical data (*193, 426*). It must be borne in mind that these results are not necessarily typical. Not enough samples of citrus lipids have been analyzed to show what variations in composition may be expected.

TABLE 14.—*Composition of lipids from Florida Valencia orange juice*

Constituent	1947	1950
	Percent	*Percent*
Unsaponifiable matter	14.81	16.53
Resin acids	12.41	10.31
Fatty acids, free	21.00	34.30
Fatty acids, combined, exclusive of those in phosphatides	13.60	3.42
Sterol glycoside	1.48	4.93
Volatile in steam	.17	
Lecithin	15.30	15.25
Cephalin	18.00	12.65
Total	96.77	97.39

The approximate total fatty acid composition, as methyl esters, of Florida Valencia orange juice lipids, based on one study (*423*), is as follows:

Constituent	*Percent*
Conjugated diene	1.3
Conjugated tetraene	.1
Conjugated triene	.2
Linoleate	32.5
Linolenate	8.8
Myristate	.5
Oleate	18.1
Palmitate	18.8
Palmitoleate	10.4
Stearate	1.7
Unidentified, molecular weight 344	1.4
Not determined	6.2

Both the rind (*276*) and pulp (*281*) of oranges contain lipids. In the former were found oleic, linoleic, linolenic, palmitic, and stearic acids and glycerol, phytosterolin, and ceryl alcohol, along with small amounts of a resin and coloring matter. The pulp contained oleic, linoleic, linolenic, palmitic, and stearic acids and probably cerotic acid, along with pentacosane, glycerol, phytosterol, and phytosterolin. Later work (*425*) identified this phytosterolin as very likely being β-sitosteryl-d-glucoside. The lipid composition of the pulp and rind appears to be rather similar, except that ceryl alcohol is present in the rind but not in the pulp, and pentacosane is present in the pulp but not in the rind.

Some work has been done on the behavior of lipids in the juice during pasteurization (*193*) and storage (*194, 195*). Pasteurization apparently causes a slight decrease in the amount of unsaponifiable matter in the lipids. Storage of canned pasteurized orange juice at room temperatures, however, causes a progressive hydrolysis of the phosphatides with the liberation of the phosphorus- and nitrogen-containing portions of these substances. These fragments are water soluble and are lost to the lipids. Storage changes in the fatty acids are minor, but lipids from canned juice after long storage show increased peroxide values and other evidences of rancidity. This discovery led to the belief that these rancidity changes in the lipid fraction might be factors in flavor deterioration of canned citrus juices (*171, 317*), but it has since been shown that other constituents are probably more important (*36, 424*).

Pectic Substances

These substances are among the most abundant and universally distributed constituents in the plant kingdom. They are found principally in the middle lamellae of plant tissues between adjoining cell walls, where they are believed to function as a "cementing" material, binding cells together (*222*).

The complexity of pectic substances, their fundamental importance in the metabolism of plants, and their usefulness to man (viz, jelly manufacture) have stimulated a great volume of research, resulting in the publication of over 2,000 papers and several hundred patents. It is not within the scope of this section to give more than a brief introduction to the pectic substances and their most important properties. Readers with more than a casual interest in these constituents should refer to the definitive monograph on this subject (*222*).

Pectic substances are a family of complex colloidal carbohydrates consisting of polymerized galacturonic acid, a sugar acid closely

related to the sugar galactose. The free acid radicals of galacturonic acid may or may not be esterified with methanol, and the degree of esterification is an important variable that markedly affects the properties of the pectic substances and is a factor in classifying them into different groups. The pectic substances include only those polymers of galacturonic acid that are colloidal by virtue of their large molecular weight. However, within this category many variations in average molecular weight, degree of esterification with methanol, and other characteristics may occur. A uniform, self-defining nomenclature for all pectic substances has been formulated and adopted by the American Chemical Society (*223*). The official nomenclature is as follows:

Pectic substances: This is a group designation for those complex colloidal carbohydrate derivatives that occur in, or are prepared from, plants and that contain a large proportion of anhydrogalacturonic acid units, which are thought to exist in a chainlike combination. The carboxyl groups of polygalacturonic acids may be partly esterfied by methyl groups and partly neutralized by one or more bases.

Protopectin: This term is applied to the water-insoluble parent pectic substance that occurs in plants and that, upon restricted hydrolysis, yields pectinic acids.

Pectinic acids: This term is used for colloidal polygalacturonic acids containing more than a negligible proportion of methyl ester groups. Pectinic acids under suitable conditions are capable of forming gels (jellies) with sugar (65 percent) and acid or, if suitably low in methoxyl content, with certain metallic ions. The salts of pectinic acids are either normal or acid pectinates.

Pectin: The general term pectin, or pectins, designates those water-soluble pectinic acids of varying methyl ester content and degree of neutralization that are capable of forming gels with sugar and acid under suitable conditions.

Pectic acid: This term is applied to pectic substances that are mostly composed of colloidal polygalacturonic acids and essentially free from methyl ester groups. The salts of pectic acids are either normal or acid pectates.

An examination of this nomenclature will disclose that both pectin and pectic acid are extreme cases of pectinic acids. In the former 55 to 70 percent of the carboxyl groups contain methyl ester groups, whereas pectic acid is practically free of methyl ester groups. The pectinic acids also include a class of commercially important pectic substances known as low-ester or low-methoxyl pectins (p. 56). Low-ester pectins are pectinic acids in which less than 50 percent of the carboxyl groups are esterified, and are characterized by their ability to form gels on the addition of bivalent metal ions, such as calcium, to their solutions (*208*). However, some bivalent metal ions, such as copper, also will precipitate pectin.

Pectic substances, being exceedingly complex organic compounds, exhibit many properties and reactions, and perhaps the most important practical property is their ability to form gels (jellies) with sugar and fruit acids (*183, 222*).

All pectic substances are precipitated as gelatinous or flocculent precipitates in 50-percent acetone or 65- to 70-percent alcohol, and they may also be precipitated or "salted-out" by high concentrations of divalent or trivalent metals, properties used in the commercial production of pectin. The insolubility increases with decreasing methyl ester content, so that low-ester pectinic acids and pectic acid may actually be precipitated as gels by mere traces of these metal salts. Pectic substances are hydrophilic colloids and as such are good emulsifiers. It is thought that the presence of pectic substances extracted into citrus and tomato juices during manufacture helps to suspend and stabilize other colloidal particles of the juices forming the desirable turbid "cloud," which bears the characteristic color of the juice.

One important problem of the citrus industry involves the action of pectic enzymes (p. 44) in improperly pasteurized juice and in frozen concentrate that has thawed, whereby the pectic substances are probably demethylated and otherwise altered so that they no longer act as emulsifiers. As a consequence the cloud of the juice breaks up and settles out, leaving an unsightly clear serum on top of the juice with a coagulated mass forming at the bottom. This phenomenon, known to the trade as cloud loss, has been a stimulus for much research on the pectic substances and pectic enzymes in citrus and tomato products.

The esterified pectic substances are readily deesterified by dilute bases at room temperature, by hot acid, and by the action of the enzyme pectinesterase. Pectic substances also undergo a peculiar, poorly understood oxidative reaction in the presence of peroxides or in the presence of ascorbic acid (vitamin C) and atmospheric oxygen. This reaction is potentially important, as it can, under suitable conditions, lead not only to the degradation of pectins in food products but to the loss of vitamin C as well (*93, 222*).

There are many methods for determining the amounts of pectic substances in plant tissues and in food products (*183, 222, 257, 325*). These methods are usually laborious and time consuming. They employ alcohol precipitation

and weighing, demethylation by a base and precipitation by calcium salts, measurement of the acid groups by titration or by decarboxylation with hot acid followed by determination of the carbon dioxide liberated (*472*), and measurement of the colored complex formed with the compound carbazol and sulfuric acid (*95*).

As with all other physiological constituents of plants, there must be enzymes capable of bringing about the formation and transformation of pectic substances necessary for their metabolism.

Briefly the four known types of pectic enzymes whose activities have been demonstrated in vitro are as follows:

(1) Polymethylgalacturonase, which is capable of hydrolyzing the glycoside bonds of fully or highly methylated pectic substances to yield degraded polymethyl-polygalacturonides (*387*).

(2) Pectin-polygalacturonase, which is found principally in molds and is capable of bringing about a limited hydrolysis of the glycoside bonds of pectin and which completely hydrolyzes pectic acid to its monomer, galacturonic acid.

(3) Pectic acid-depolymerase, found principally in tomatoes and also reported in grapefruit (*338*), which causes a rapid loss of molecular weight of low-ester pectins and pectic acid with a relatively small degree of hydrolysis of glycoside bonds.

(4) Pectinesterase, or pectin-methylesterase, found both in molds and in higher plants, including citrus, which catalyzes the hydrolysis of the methyl ester bond, yielding from pectinic acids, pectic acid and methanol (*222, 224*).

The pectic enzymes peculiar to citrus fruits are discussed more fully in a separate section (p. 6).

Pectic substances appear to occur in situ, principally in the form of protopectin, although significant amounts of low-ester pectinic acids are also found in the middle lamellae, and varying amounts of soluble pectinic acids and pectin are found in the cell sap and other parts of plants. Pectic substances appear to be laid down in the greatest amount during the early growing stages of the plant or of the fruit, and are believed to undergo a definite pattern of changes during fruit ripening. Presumably unripe fruit is rich in protopectin and contains little of the other pectic substances. The insolubility of protopectin in the middle lamellae is believed to account for the firmness of unripe fruit. As fruit ripens it is thought that protopectin is broken down by the action of an assumed enzyme protopectinase, which has yet to be demonstrated in vitro, to soluble pectins and pectinic acids and causes softening (*93, 183, 210, 222*). Much work has been carried on to establish the cycle of ripening and softening of fruit, with somewhat inconclusive results. However, it does seem clear that usually in fruit ripening a general trend can be shown to exist of a reduction in molecular weight of the pectic substances present, even though it is not always possible to demonstrate a decrease in total pectic substances or an increase in soluble pectic substances.

Among the richest sources of pectic substances in the plant kingdom are apples and citrus fruits (*183, 222*). The edible portions of the apple are rich in pectic substances, containing from 0.5 to 2.0 percent on a fresh-weight basis. Both the peel and the pulp of citrus fruits are rich sources of pectic substances, including protopectins. The flavedo and albedo of citrus fruits contain the greatest amounts, having from 20 to 40 percent on a dry-matter basis. The pulp of citrus fruits, on the average, will contain one-half to one-third of the amount of pectic substances found in the peel portions.

Vitamins

Vitamins are a group of organic substances required in minute amounts as a component of the diet for normal health and well-being (*487*). Many of the vitamins have been isolated as pure compounds, which have been characterized, and some have been synthesized. These vital chemical compounds consist either of groups of related individuals or of complexes of unrelated compounds having diverse physiological activities. Different vitamins have little in common so far as chemical structure is concerned. Some are sugar acids, some are sterols; some contain nitrogen, others do not. Therefore, vitamins are not, as originally supposed, necessarily amines.

In general, vitamins are not synthesized by the animal body, and therefore must be obtained from an outside source. They do not furnish energy, and they are not utilized as building units for growth of the organism. Although they are present in relatively small amounts, vitamins perform specific and vital functions, and are essential for the transformation of energy and the regulation of metabolism. Certain vitamins function as prosthetic or action groups in the enzyme systems that control cell respiration and intracellular respiration. Others have specialized functions not critically related to basal metabolism (*26*).

Vitamins differ from other well-known essential nutrients in several ways. First, the amounts required are much smaller than are the requirements for proteins, carbohydrates,

fats, and minerals. Second, they may be inactivated by heat, light, chemicals, and heavy metals. Third, they may exist in inactive forms as provitamins, which require special enzymatic or chemical treatments before they become physiologically active. For example, the carotenoid pigment β-carotene, present in many foods, must first be converted to vitamin A by the animal body before it becomes physiologically useful.

Vitamins are generally separated into two groups, those that are fat soluble and those that are water soluble. The early discovered vitamins were designated by letters of the alphabet, because little was known regarding their chemical identity. Some received descriptive names, whereas others have been renamed as their chemical structures have been established.

In the early days of vitamin research the presence or absence of a particular vitamin was determined by feeding experiments with such test animals as the rat, guinea pig, dog, and chick. These tests are known as bioassays, in which the presence and amount of vitamins are expressed in terms of animal response. For example, the original unit of vitamin C was the smallest amount that would prevent development of scurvy in a guinea pig. Bioassays to estimate the vitamin content of foods or other materials are costly, tedious, and time consuming. They have now been superseded by numerous chemical, microbiological, and physiological methods (*174, 409, 448*).

The demand for and acceptance of citrus fruits in the daily diet of humans is based largely on their nutritional value and particularly on their vitamin C content. Although vitamin C (ascorbic acid) was not isolated from lemons until 1932 and its structural formula was established a year later, the effectiveness of citrus juices in alleviating scurvy was recognized in the 1700's. In 1757 Dr. James Lind, a surgeon in the British Navy, published a Treatise on Scurvy, in which he described this dread disease and recommended means for preventing and curing it, confirming the theory that scurvy was due to a shortage of fresh fruits and vegetables in the diet. Later the British Navy made lemon or lime juice a compulsory ration as a preventive measure against scurvy during long sea voyages.

The vitamin C content of citrus juices may vary widely with fruit variety, stage of maturity, climate, soil condition, geographic location, and related factors (*144, 145, 147, 148*).

A compilation of the available data on the vitamin content of fresh and heat-processed juices from orange, grapefruit, tangerine, lemon, and lime is presented in table 15. In general, the average retention of vitamin C during the canning process is about 97 percent, with an average loss of 1 to 2 percent per month during storage at room temperature (*111, 121, 244, 288, 294, 295, 298-300, 302, 341-343, 363, 364, 462, 474*). Loss of vitamin C in canned pasteurized fruit juices appears to be closely related to storage temperature; lowering the storage temperature effectively protects the vitamin (fig. 3). Citrus juices also contain small but significant amounts of provitamin A, B-vitamins, and other factors for which human requirements have not been established. The data in table 15 appear to indicate that biotin, folic acid, inositol, and niacin are among the more stable B-vitamins, whereas losses of thiamine, riboflavin, pantothenic acid, and β-carotene occur in heat-processed citrus juices. It has been reported that losses of thiamine in citrus juices are effectively reduced by lowering the processing and storage temperatures.

Freshly extracted orange or grapefruit juice will retain from 96 to 99 percent of its original vitamin C content for at least 1 week when stored at 40° F. (*296*). The length of time such orange or grapefruit juice may be allowed to stand before use appears to be limited by loss of palatability and beginning of fermentation, not by appreciable vitamin C loss.

There seem to be no significant differences in vitamin potency between freshly squeezed orange juice and reconstituted frozen concentrates, although published data indicate that frozen concentrated juices on an average are slightly higher in vitamin C, β-carotene, and vitamin B_{12}, and that the freshly squeezed juice contains on an average slightly more pyridoxine and inositol (*350, 351*). A survey of the vitamin C content of 20 commercial brands of frozen concentrated orange juice has been reported (*6*). After reconstitution, the vitamin C values showed wide variations between minimum and maximum values for most of the brands studied. The averages ranged from 30 to 46 mg. per 100 ml. of reconstituted juice, with an overall average of 42 mg. The amount of vitamin C varied from 30 to 50 mg. per 100 ml. within a single brand to an overall difference of 29 to 52 mg., representing the extremes among the 20 brands studied. In another study (*288*) frozen concentrated orange juice was reconstituted and stored from 4 to 8 days at 32°, 41°, and 77° F. Those samples held at 32° for 8 days and at 41° for 4 days suffered no impairment of flavor and minimum loss of vitamin C. However, at 77° palatability was lost before any significant loss of vitamin C occurred. These results confirm an earlier investigation (*296*), which demonstrated that orange juice stored at icebox temperature will become unpalatable before any significant destruction of vitamin C occurs.

TABLE 15.—*Vitamin content of fresh and heat-processed canned citrus juices* [1]

Vitamin	Other designation	Units per 100 ml.	Orange		Grapefruit		Tangerine		Lemon		Lime	
			Fresh	Processed	Fresh	Processed	Fresh	Processed	Fresh	Processed	Fresh	Processed
Provitamin A	β-Carotene	International units	190–400	2–160	(2)–21	0–15	350–420		0–2	0–2		
B_1	Thiamine	Micrograms	60–145	30–100	40–100	10–50	70–120	60	30–90	40	40	
B_2	Riboflavin	do	11–90	10–40	20–100	5–30	30	30	60	5–50	(2)	(2)
B_6 group [3]		do	25–80	16–31	10–27	7–27	23	33				
B_{12}	Animal protein factor	do	.0011–.0013									
B_c	Folic acid, folacin, pteryl-glutamic acid.	do	1.2–3.3	1.5–3.2	.8–1.8	.1–2.2	1.2	1.8				
Bios I	Inositol	Milligrams	98–210	104–178	88–150	92–112	135	147	85			
Biotin		Micrograms	.10–2.0	.5–1.1	.4–3.0	.3–.9	.5	.5				
C	Ascorbic acid	Milligrams	35–56	34–52	36–45	32–45	25–50	26–31	45–60	30–58	27	
Choline		do	10–13									
E	Tocopherols	do	88–121									
Factor II	Pantothenic acid	Micrograms	130–210	60–200	290	70–190						
K	Antihemorrhagic factor		0									
PABA	Para-aminobenzoic acid	Micrograms	4									
P-P	Niacin	do	200–300	170–300	200–220	80–200	200–220	200	100–130	80–100	100	

[1] Compiled from various published data.
[2] Trace.
[3] Includes pyridoxine, pyridoxal, and pyridoxamine.

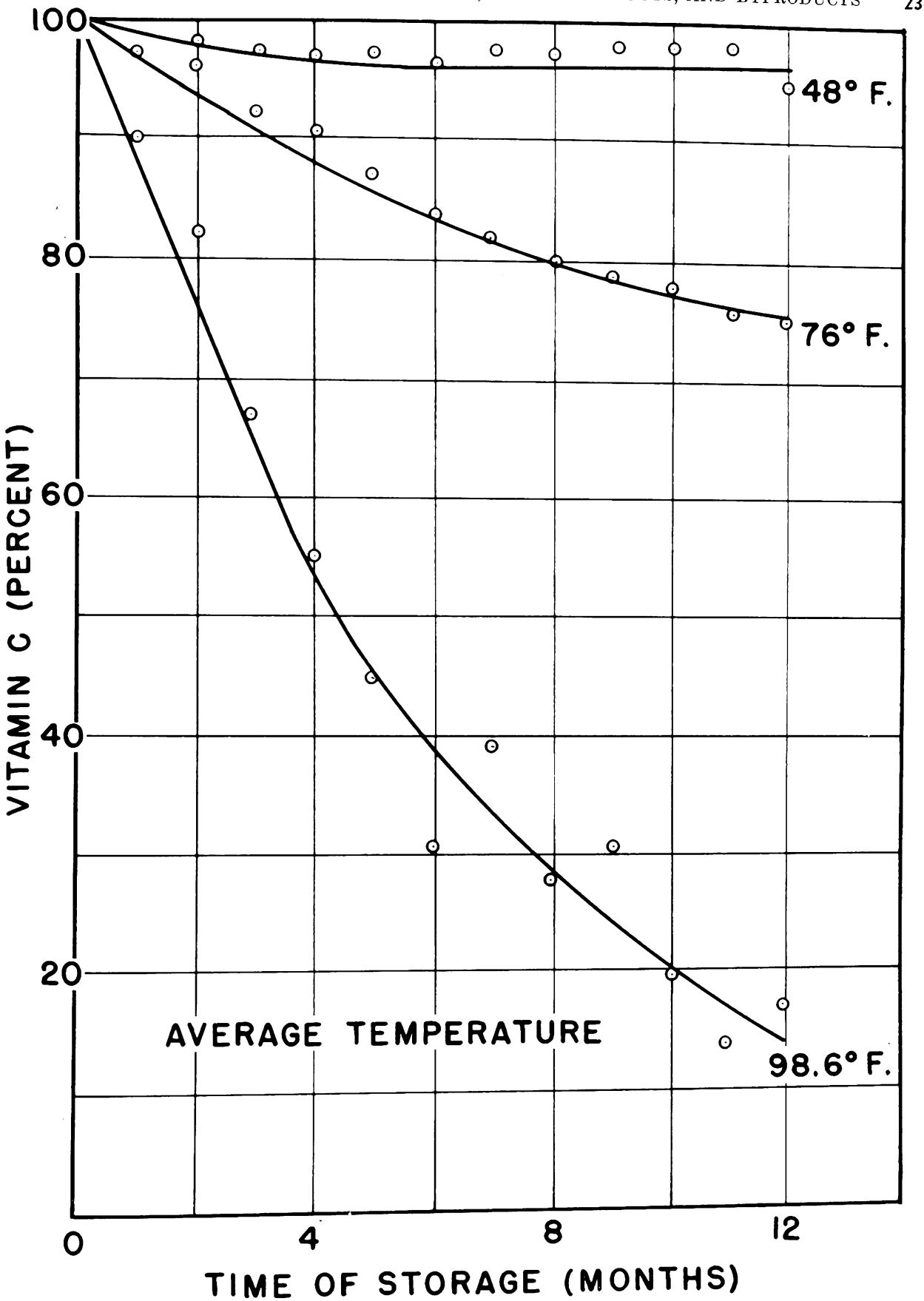


FIGURE 3.—Vitamin C retention in canned orange juice under different storage temperatures (adapted from Ross (*364*)).

Frozen concentrated orange juice is a rich source of vitamin C. An average loss of only 3.4 percent of the original vitamin C content has been observed during the preparation of frozen concentrates from single-strength juice (*159*). Losses during storage of frozen concentrates at 0° F. for a year are generally less than 10 percent (*70*). Vitamin C is retained for nearly a week in frozen concentrates held in the common household refrigerator, whether they are left in the can or reconstituted into single-strength juice. At 41° losses of vitamin C were not serious in 4 days (*288*). Even though samples may have deteriorated extensively so far as flavor, gelation, and loss of cloud are concerned, the vitamin C content may remain substantially unchanged.

Inorganic Constituents

Inorganic constituents of citrus juices comprise what is known as the ash, the material left after all organic material has been destroyed. The recovered ash is composed of the neutral salts in the juice plus carbonates formed by the decomposition of organic acid salts, the so-called alkaline ash. Table 16 is a compilation from various sources of the ash constituents of citrus juices. Ash will vary with the pressure used to juice the fruit and with the amount of pulp left in the juice. In addition to analytical variables, these values depend on such factors as type of soil on which the fruit is grown, fertilizer practices, location of the groves, region of growth, rootstock on which the trees are grafted, variety of fruit, and the season during which the fruit is harvested.

Potassium accounts for 60 to 70 percent of the total cation content of the juice. It is probable that most of this element is tied up in the form of potassium acid citrate (*395*). The major portion of the calcium and magnesium is in a water-insoluble form combined with pectin.

Phosphates, sulfates, chlorides, and nitrates are some of the anions that combine with a portion of the cations (*395*). Bromine, fluorine (94 μg. per 100 ml. in orange juice), and iodine are present in citrus juices, probably in the form of salts (*42, 350, 412*). Borates are also found in citrus juices, orange juice particularly containing a surprisingly high amount—0.05 to 0.33 mg. of boric acid per liter.

Other elements detected in citrus juices in trace amounts are aluminum, nickel, barium, chromium, copper, tin, manganese, vanadium, silicon, lead, strontium, titanium, zinc, and zirconium. The fact that citrus juices contain copper (0.3-0.9 p. p. m.) is important, because it has a role in the destruction of ascorbic acid.

Nutritionally the elements copper, iron, iodine, manganese, and zinc are considered of significance, since these cations are associated with basic enzyme systems concerned with metabolism in the human body. The relatively low sodium content of citrus juices is of particular dietetic interest, because low sodium diets are important in treating various chronic conditions, such as cardiac diseases. Citric acid is almost completely oxidized in the body. This is important, because citric acid salts of the juice are metabolized on ingestion, liberating the combined cations and thus helping to maintain the alkaline reserve of the body.

PROCESSING OF CITRUS

Canning

ORANGE JUICE

The annual pack in the United States of canned single-strength orange juice has been approximately 20 million cases. Certain varieties are preferred for canning. The Pineapple orange in Florida is considered excellent; many seedling trees produce top-quality fruit for juice. The Valencia orange is unsurpassed in both Florida and California for color as well as fine flavor. The flavor and appearance of the freshly extracted juice are generally good indications of its suitability for canning. Washington Navel oranges produce a juice that sometimes becomes bitter (*108*). Overmature, undermature, or stale oranges (fruit that has stood too long after picking) do not make good juice (*459*).

TABLE 16.—*Total ash and ash constituents of some citrus juices*

Citrus juice	Ash	Calcium	Chlorine	Iron	Magnesium	Phosphorus	Potassium	Sodium	Sulfur
	Gm. per 100 gm.	*Mg. per 100 gm. of ash*	*Mg. per 100 gm. of ash*	*Mg. per 100 gm. of ash*	*Mg. per 100 gm. of ash*	*Mg. per 100 gm. of ash*	*Mg. per 100 gm. of ash*	*Mg. per 100 gm. of ash*	*Mg. per 100 gm. of ash*
Marsh grapefruit, Florida (*42*)	0.4	8	1	0.1	5	10	90	4	2
Seedy grapefruit, Florida (*362*)	.4	15	2	.08	9	29	172	7	4
All varieties of lemon, California (*20*)	.3	26	3	.35	10	13	164	21	7
Valencia orange, California (*412*)	.4	14	6	.25	13	20	170	6	8
Valencia orange, Florida (*362*)	.4	9	3	.1	5	32	172	7	4
Tangerine, Florida (*362*)	.4	12	3	.28	7	15	177	6	6

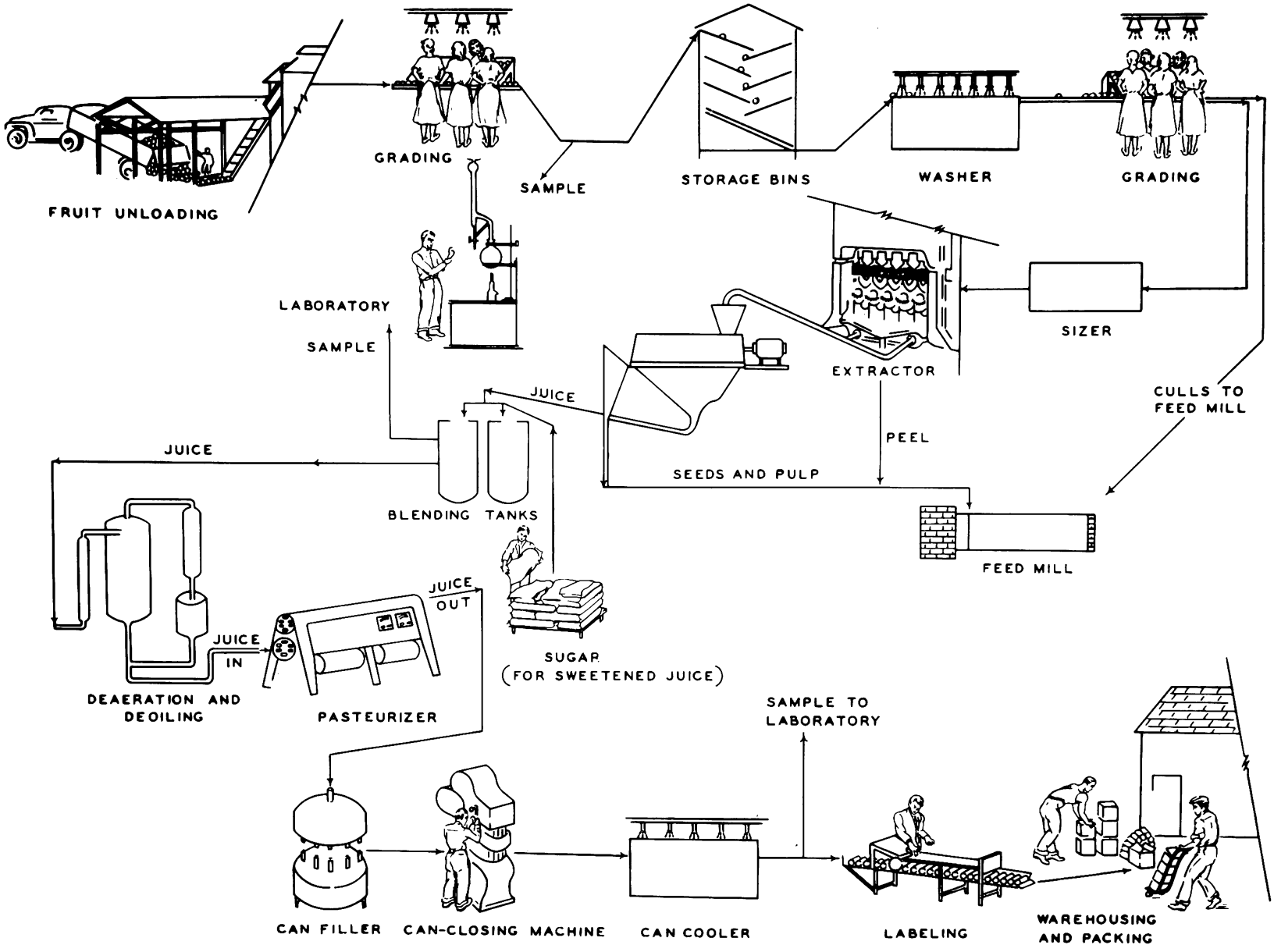


FIGURE 4.—Flowsheet showing steps in the canning of single-strength orange juice.

Fruit is delivered to the canning plants by trucks holding from 35,000 to 40,000 pounds. At the plant it is unloaded for inspection and grading, and unsuitable fruit removed before the oranges are run into storage bins prior to canning (fig. 4).

An automatic sampler removes some of the oranges at this point for determination of soluble solids and acid. By knowing the ratio of soluble solids to acid for oranges in each bin, fruit from various bins can be blended to produce juice of more uniform flavor. The bins also provide a supply of fruit for continuous operation.

As the fruit comes from the bins, it is carefully scrubbed with a detergent on a rotary brush washer and rinsed with potable water. It is again inspected and damaged oranges are removed.

Plants processing orange juice are equipped at several points with facilities for the inspection and discarding of damaged fruit. A convenient arrangement is to pass the oranges over a roller conveyor so that all sides of the fruit are exposed. These roller conveyors or grading tables are well lighted, installed at a convenient height, and of such width that all fruit can be reached by the inspectors. For adequate inspection fruit should not cross the grading tables at a rate in excess of 30 feet per minute (*43*). Causes for rejection include ruptured peel and evidence of mold or rot. Examination of the juice in the control laboratory is helpful in revealing the effectiveness of the grading.

Prior to juice extraction, the oranges must be separated according to size, and this is accomplished by machines that may be purchased from most canning-supply manufacturers.

Several effective juice extractors (figs. 5 and

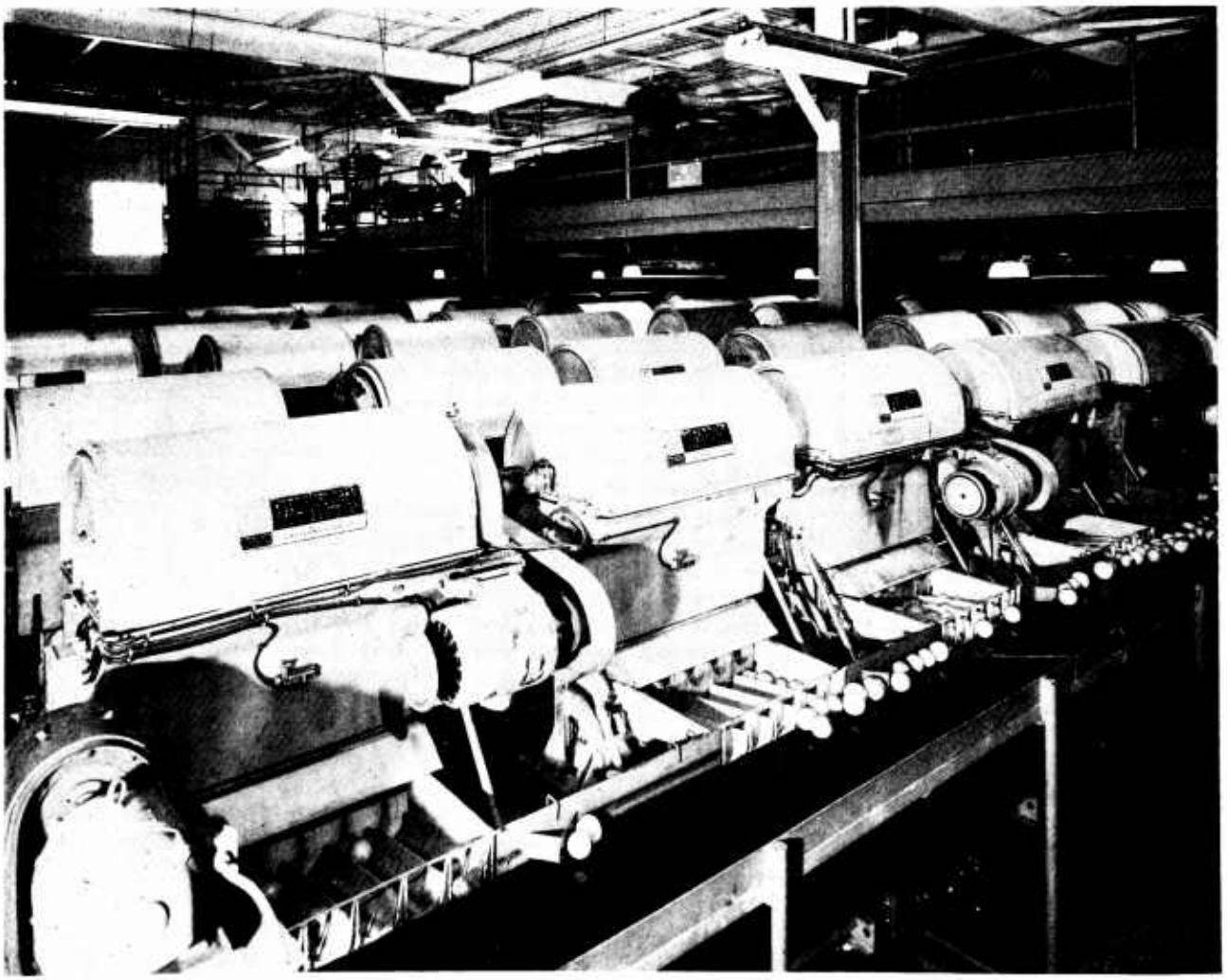


FIGURE 5.—Assembly of juice extractors in a citrus-processing plant. (Courtesy of Florida Citrus Canners Coop., Lake Wales, Fla.)

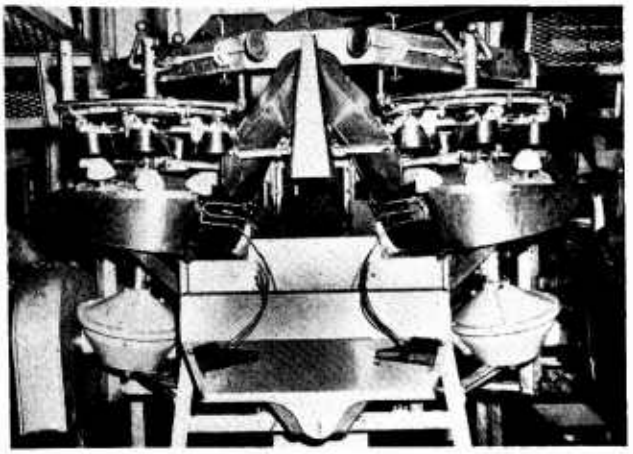


FIGURE 6.—Another type of juice extractor. The guards have been removed to show the heads for extracting the juice from the fruit.

6) are employed by the industry and operate in various ways. Some halve the fruit and remove the juice by reaming or by pressing; one machine inserts a tube through the peel, and by squeezing the whole fruit it forces the juice out through the tube. Although extracting machines may differ in design and are rather complicated, they all possess certain features in common. They are fast, rugged, easily cleaned, and can be adjusted to reduce the incorporation of peel extractives into the juice. The canner usually leases extracting machines from the manufacturer on a royalty basis.

Extracted juice is free from peel, but may contain seeds and coarse pulp. These are removed by finishers, which vary in design. One, of a screw-type design, consists essentially of a conical helical screw enclosed in a cylindrical screen with 0.020- to 0.045-inch perforations.

The finished juice flows into blending tanks, where it is tested for soluble solids and acid. The juice may be packed unsweetened, or sugar may be added at this point to make sweetened orange juice for canning. The requirements for soluble solids, acid, and color are given in detail in the United States Standards for Grades of Canned Orange Juice (*446*).

After blending, the juice is deaerated (fig. 7). As practiced today deaeration is often accomplished in the same operation as deoiling. Air incorporated in the juice during extraction and finishing can be effectively removed by an apparatus developed for the purpose (*303, 344, 347, 459*). There are several benefits from deaerating orange juice, such as improvement in uniformity of can fill by elimination of foaming in the filler bowl; improvement in efficiency of the heat exchanger with less danger of scorching the juice; and when enamel-lined

FIGURE 7.—Pulley-type deaerator (U. S. Public Service Patent No. 2,060,242) for citrus juices. (Courtesy of American Machinery Corp., Orlando, Fla.)

cans are used, less separation of enamel from the cans (*358*).

Excessive amounts of peel oil in the juice may be objectionable. However, some peel oil is considered necessary for maximum flavor (*85, 358*), and according to the United States Standards for Grades of Canned Orange Juice it may contain up to 0.030 percent of recoverable oil (*446*). To control the amount of peel oil in the juice, deoiling sometimes becomes necessary, and this may be accomplished by vacuum distillation (*346*). After condensation, the oil can be separated and the aqueous distillate returned to the juice. There are several deoiling units on the market, which may be purchased by the processor.

The deaerated or deoiled juice is next pasteurized. Pasteurization of single-strength orange juice, as now practiced, is not primarily directed toward the destruction of spoilage organisms. It was realized years ago that heating at temperatures as low as 150° F. is sufficient to destroy most spoilage organisms. The orange

juice thus preserved, however, separates into a clear liquid with a sediment at the bottom. Evidently after the spoilage organisms are destroyed, the juice is subject to another type of deterioration, and it was found that heating to higher temperatures (up to 200°) conferred additional stability. It was later realized that these chemical changes were brought about by the presence of naturally occurring enzymes, and the recommendations for heating to 190°-200° reflect a better understanding of the problem of stabilization. Today it is recognized that the particular enzyme pectinesterase (p. 6) may be associated with deterioration, and processing is directed to the conditions necessary for destruction of its activity. A simple test has been devised (*228*) to check the efficacy of the pasteurization process by testing for the activity of pectinesterase.

In present commercial practice the juice is rapidly heated to about 197° F., the exact temperature being dependent somewhat on the particular equipment in use and the rate of juice flow. Juice is generally in the pasteurizer for about 40 seconds.

Flash pasteurization is carried out with either tubular or plate-type heat exchangers. A study (*165*) of pasteurization of citrus juices indicated that turbulent flow is necessary to heat the juice rapidly without local overheating. Inevitable variations in the flow of juice, which could result in scorching or underheating, are reduced by the design of modern heat exchangers and automatic controls.

After the cans are filled with hot (180°-200° F.) pasteurized juice, they are inverted to allow the hot juice to sterilize the inside of the lids, and then cooled. The juice is hot during pasteurization and while the cans are filled, closed, and held inverted—a total of 2 to 3 minutes in commercial operations. Cooling to 90°-100° is accomplished rapidly by spinning the cans on a conveyor under sprays of cool water. It is desirable to have the cans emerge from the cooler with some residual heat (not more than 100°) to facilitate drying and prevent subsequent rusting.

Sometimes a jet of steam may be played beneath the can lid before sealing. This cleans the underside of the lid and aids in obtaining a vacuum in the can (*331*).

Time and temperature of storing canned juice are of prime importance in maintaining quality of the product. Modification of orange-juice flavor during actual canning is slight, and off-flavors that develop are chiefly the effects of subsequent storage temperatures. Rate of deterioration increases with increased storage temperatures, and juice should be kept as cool as economically possible.

Storage studies of canned single-strength orange juice at various temperatures and periods of time (*114, 136, 244, 299, 302, 364*) have shown that in 12 months only slight changes in flavor occur at or below 60° F.

Riester, Braun, and Pearce (*358*) state, "The importance of adequately controlled low-temperature storage cannot be overemphasized. It is difficult to conceive of an improvement in production technic, even though revolutionary, the effects of which would not be largely nullified by high-temperature storage." Many warehouses for canned citrus juices have been insulated and ventilated to maintain storage temperature as low as practical.

GRAPEFRUIT JUICE

The methods described for canning single-strength orange juice are also applicable to the canning of grapefruit juice. The main difference is that the juice extractors must be adjusted to handle the larger fruit. Sometimes canning plants are equipped with juice extractors designed to handle the whole range of fruit sizes from small oranges to large grapefruit, and therefore can switch back and forth from one juice to the other.

As previously mentioned grapefruit contains a bitter glucoside, naringin, most of which is found in the albedo, rag, and pulp (*226*); pectinesterase activity is also associated with the solid material (*262*). Consequently, in extracting the juice and separating it from the solid portions efforts are made to minimize the extraction of naringin and the incorporation of too much pulp (*358*).

There is no general agreement on the value of deaeration for grapefruit juice.

Pasteurization is concerned with the inactivation of pectinesterase (*326*), just as in the processing of orange juice. The same rapid test (*228*) for residual enzyme activity as an index of pasteurization will be helpful.

Canned grapefruit juice is an excellent source of vitamin C, and its retention during processing (*298*) and in storage is similar to that observed with canned orange juice (*244, 299, 302, 364*).

BLENDED JUICES

Blended grapefruit and orange juice is produced by the procedure described for orange and grapefruit juices, except for the blending. The general practice is to use approximately equal quantities of the two juices. However, when the oranges yield light-colored juice, the proportion of orange juice is increased. Late in the season when more deeply colored juice is available, the proportion of orange juice is

decreased. It is desirable to keep the appearance and flavor as uniform as possible over the entire season.

Canned blended grapefruit and orange juice of United States grade A may contain 0.030 percent by volume of recoverable oil (*444*).

Canned blended juices are excellent sources of vitamin C, as about 98 percent of the vitamin is retained during canning; retention in storage is equal to that of either juice canned separately (*372*).

Tangerine-orange blends have a good flavor, but cannot compete on the market with grapefruit-orange blends because of economic reasons.

TANGERINE JUICE

Despite earlier difficulties (*11*) it has been found (*79*) that an acceptable canned single-strength tangerine juice can be produced. An important factor in preparation appears to be avoiding excessive extractives from the pulp and peel. Tangerine juice should contain not more than 0.020 percent of recoverable oil and not over 7 percent of free and suspended pulp (*440*).

Since the fruit is fragile, it is usually delivered to the plant in boxes rather than in bulk by trucks. The fruit is conveyed directly into wash tanks, bypassing the storage bins. Processing is similar to that described for producing canned single-strength orange juice. Extractors must be specially adjusted to handle the smaller fruit.

LIME JUICE

There are only two acid fruits of the lime group *Citrus aurantifolia* (Christm.) Swingle that have attained commercial importance. These are the Key (Mexican or West Indian) lime, a small round fruit averaging about 1 inch in diameter, and the Persian (Tahiti) lime, which is considerably larger, being about the shape and size of the commercial lemon. These fruits are very acid and contain from 5 to 8 percent of citric acid.

Only a limited amount of canned lime juice has been marketed largely because of changes that take place in appearance and flavor at room temperature. The procedures of preservation have been based on those commonly used in processing canned orange juice. Use of the Persian variety has permitted extraction of juice with standard juicing equipment. The juice, after passing through a finisher, is pasteurized at about 195° F., filled into cans, and cooled. Refrigeration at 35° greatly extends its storage life; samples have been stored as long as 15 months at this temperature (*34*) without appreciable deterioration.

Since the Key, or Mexican, lime is smaller than the Persian, the use of conventional juice extractors is impracticable; therefore, juice is generally extracted by crushing the whole fruit in a screw press. The juice obtained may have a high oil content, but this can be reduced by vacuum deoiling. Sometimes lime juice is clarified by mixing with a filtering aid and filtering in a plate-and-frame press. This clear juice is used in compounding formulas for bottled drinks and fountain use.

Lime oil, both cold-pressed and distilled, is usually a byproduct of juice manufacture. The peel is used for recovery of cold-pressed and distilled oil, and the filter cake from clear-juice production may be used for distilled oil.

In the West Indies lime juice is prepared by crushing the whole fruit as in the preparation of oil, except that stone rollers are used. The expressed juice is screened through a 3/16-inch mesh screen and then through a 1/8-inch mesh. It is pumped into wooden storage tanks, where it is allowed to remain for 16 to 30 days. During this period a sludge settles to the bottom and light pulp rises to the surface. Fermentation is retarded by the high acidity and low sugar content of the juice; the oil present also acts as an inhibitor of fermentation.

After the pulp settles, the intermediate clear layer of juice is drawn off, filtered through cloth, and stored in paraffin-lined barrels holding from 50 to 100 imperial gallons. Sulfur dioxide (350 p. p. m.) or 0.1 percent of sodium benzoate is added, depending on the import regulations of the country to which the juice is to be sent.

In commerce the following types of West Indian lime juice are recognized (also see p. 37):

(1) "Settled" or "racked" juice. This is the clear juice obtained as previously described. It should be clear and sparkling and with a typical lime flavor. Often it has a peculiar musty lime flavor quite different from lime juice prepared in the United States. This peculiar flavor is very acceptable to the British palate; in America it is not so widely accepted. The acidity of this type of juice should run from about 9.4 to 12 percent, calculated as anhydrous citric acid.

(2) "Top juice with pulp." This contains light fine pulp and oil floating as a thin film on the surface. Most of this juice is used in the West Indies for making distilled lime oil.

LEMON JUICE

The commercial production of lemon products in the United States is confined almost

exclusively to California. The Eureka lemon is the principal variety grown, comprising approximately 88 percent of the total production. Lisbons make up about 8 percent of the total, and miscellaneous varieties comprise the remainder. The lemon industry in California is unique in that the fruit is picked for size only and held under controlled storage conditions to undergo coloring from green to yellow instead of being left on the trees to color. Lemons sorted at the packinghouses may be used as the raw material for processing, although under unfavorable market conditions large tonnages of grove-run fruit may be diverted from the fresh market to processing.

In preparing natural single-strength lemon juice, the initial operations of fruit handling, inspection, washing, sizing, and extraction of the juice are the same as those described for other citrus juices. After the juice is extracted from the fruit and screened to remove rag and seeds, it is usually held in storage tanks for a short time for the purpose of blending. If the juice is to be frozen, brine-jacketed tanks are used to chill the juice. When required, the juice can be deaerated in these tanks by applying a vacuum of 20 to 25 inches of mercury for about 30 minutes.

At least six lemon-juice products are now being manufactured in California, including pasteurized or frozen single-strength juice, concentrate, and lemonade concentrate.

In the preparation of *canned frozen single-strength juice,* the chilled juice is drawn from the coldwall holding tanks and further cooled to 30° F. by passage through a heat exchanger. It is then filled into cans, sealed, frozen, cased, and stored at 0° to –10°.

In the preparation of *canned pasteurized juice,* the juice is generally centrifuged to remove a portion of the solid suspended material and then pumped through deoilers, where a large portion of the volatile oil is flashed off by heating the juice to approximately 175° F. for a short time. The presence of this oil would create off-flavors in the canned product. This treatment also stabilizes the cloud and pasteurizes the juice. The hot (175°-180°) juice is filled directly into cans, sealed, cooled as rapidly as possible with cold water, and cased. No further processing is necessary. The filled cases are usually stored at around 40° to prevent changes in the product, which occur too rapidly at higher storage temperatures. The principal deterioration of lemon juice is a browning of the juice, resulting in an off-flavor and poor appearance. Cool storage retards this change.

Large amounts of single-strength *bottled lemon juice* are produced. This product is not made from the natural single-strength juice previously described, but by reconstituting a concentrated lemon juice. Either pasteurized concentrates (p. 35) or frozen concentrates are generally used. Several reasons have been given for using reconstituted lemon juice instead of the natural juice in making this product. The most important is uniformity of quality. For example, the acid content of the reconstituted juice is controlled by blending to insure uniformity from bottle to bottle. A longer shelf life is reported for this product. Decentralized bottling plants convenient to major markets may be established, in which case it could be more economical to ship the concentrate to be reconstituted at the bottling plant than to ship the natural-strength juice. If the concentrate has not been heated, it is pasteurized at approximately 176° F. for 1 minute to stabilize the cloud.

Water that is purified through carbon filters and deaerated in a vacuum tank is added to the concentrate to reconstitute it to natural strength. The reconstituted juice is then homogenized at about 3,500 pounds per square-inch pressure, and sufficient sodium benzoate or sulfur dioxide added as a preservative. The juice is filled into bottles (usually green in color) and capped. No artificial coloring or flavor is added. The presence of sulfur dioxide or sodium benzoate must be declared on the label in accordance with regulations of the Federal Food, Drug, and Cosmetic Act.

GRAPEFRUIT SECTIONS

Seedy grapefruit, such as the Duncan, is preferred for section canning. Upon arrival at the processing plant the grapefruit is inspected, and the sound fruit is separated according to size into bins. Uniformity of size of the segments in the canned product is improved by using fruit of one size at a time. Sizes considered ideal are fruits that measure from $3^{15}/_{16}$ to $4^{13}/_{16}$ inches in diameter. Small and very large sizes are commonly used for juice production. Since part of the subsequent operations is handled on a piecework basis, small fruit is too expensive to use, and excessively large fruit yields too few segments per can.

Two methods are used for peeling the fruit (*456, pp. 61-71*). The "cold peel" method is one in which the peel is sliced off in such a manner that both the albedo and outer membrane of the segments are removed. This method results in a lower yield, and segments sometimes show excessive trimming. However, it is employed when the fruit is tender and will not stand lye peeling.

The more generally used method of peeling

FIGURE 8.—Peeling grapefruit in preparation for sectionizing. (Courtesy of American Machinery Corp., Orlando, Fla.)

is to "scald" the fruit either by steam or in water (196° -210° F.) for about 5 minutes for the purpose of plumping the peel for easier peeling. It is then cooled slightly with water sprays as it emerges from the scalding tank. Peelers deftly remove the peel (fig. 8) with the aid of a short knife by slitting or scoring the stem end of each fruit and pulling off the peel. Some of the adhering albedo is stripped off with the short blade of the knife and the thumb. A machine to peel the fruit is in an experimental stage.

Baskets of peeled grapefruit are passed through a lye peeler. Banks of sprays successively spray the grapefruit with hot (200°-212° F.) alkali of about ½- to 2½-percent concentration for about 12 seconds. A variable speed conveyor carries the baskets under about 10 feet of these alkali sprays, followed by 15 feet without treatment to allow the alkali to dissolve adhering albedo, and then under 40 feet of water sprays to rinse the fruit. The "canner's alkali" is a mixture of sodium hydroxide and sodium carbonate, which is believed to be easier to remove from the fruit by the water rinse than sodium hydroxide alone. The alkali solution from the sprays is collected in a tank under the conveyor and circulated by pumps back through the sprays. During a period of operation the dissolved fruit solids build up in the lye solution, so that it is desirable to start with a fresh solution each day or even more often. Because of such variables as changing composition of the lye solution and differences in fruit, lye peeling must be carefully controlled to obtain the desired results. This control is based largely on personal experience by observing the fruit as it emerges from the lye bath.

The peeled fruit is conveyed in baskets to sectionizing tables. Here a limited amount of fruit is allowed to accumulate for three purposes: First, the peeled fruit when warm is fragile and apt to break up during sectionizing; second, a supply ahead enables the sectionizers to work without interruption; and third, delay permits dissipation of final remnants of yellow color remaining after lye treatment.

Successful sectionizing depends on the skill and experience of the operator. The grapefruit is either held in the hand or placed on a revolving spindle inserted through the center of the fruit (fig. 9). A stainless-steel or aluminum spatula with a wide base is inserted between the fruit cells and membrane of each segment and the segment lifted out. Seeds are wiped from the

FIGURE 9.—Sectionizing grapefruit. (Courtesy of Florida Citrus Canners Coop., Lake Wales, Fla.)

segment with the edge of the spatula after the section has been transferred to the other hand, or removed by brushing or tapping two segments against each other. The sections are packed by hand into unlined cans containing the requisite amount of sirup made by dissolving sugar either in water or in juice. Density of the sirup is adjusted to give, after storage, a "cutout" (drained) sirup to conform to standard designations: Heavy sirup (18° Brix or more), light sirup (16°-18° Brix), or slightly sweet (12°-16° Brix). It is necessary for operators to wear rubber gloves to prevent skin irritation. Machines have been developed for sectionizing grapefruit, but are not as yet in extensive use.

The fruit is arranged in the cans by placing sections around the periphery in such a manner that a hole is left in the center. Whole segments and broken segments are customarily packed in separate cans and appropriately labeled. Care must be taken not to overfill the cans, as the sections may be broken when the cans are lidded, and they may appear bulged, which usually suggests spoilage to the lay person. If insufficient sections are added, a loose pack results, oxygen in the head space increases corrosion of the cans, and the packer may be penalized for slack fills (*445*).

Filled cans are either vacuum closed and processed, or exhausted by heat, closed, and processed. Vacuum closure is accomplished by injecting steam to displace the air beneath the lid as it is placed on the can. After No. 2 cans are sealed, they are heated to about 185° F. for 35 minutes in a cooker-cooler (fig. 10). If the cans are heat exhausted, the filled but open cans are conveyed through a tank, called an exhaust box, of hot (180°) water. The temperature of the sirup in the center of the cans emerging from the exhaust box should be 146°. No. 2 cans are exhausted for 27 to 35 minutes. They are sealed and heated for 16 to 30 minutes at 176° to 185°. They are then cooled to about 100° by being conveyed through a cooling tank. Cans are handled and cased as gently as possible to avoid breaking the sections. It is desirable to let the cans stay undisturbed for 10 days to 2 weeks, during which time the sections become decidely more firm.

MANDARIN SECTIONS

This product has not been commercially successful in the United States, but before World War II significant quantities of such a pack were imported from Japan. The canning method used there has been described by Boswell (*39*). The washed fruit is passed through a steam or hot-water bath for about 1 minute to facilitate peeling, and then cooled in cold water. The fruit is peeled by hand, and then is placed in shallow trays until the surfaces have dried. The sections are separated by hand, and immersed in cold (68°-77° F.) 2½-percent hydrochloric acid for about 2 hours to remove the stringy fibers adhering to the peeled fruit. The acid is subsequently removed in running water. The washed segments are immersed for 25 minutes in a 1-percent solution of sodium hydroxide at 113° and then again washed. The cans are filled with these sections, and are subsequently inverted to drain off excess water. Each can contains 325 gm. (11.46 ounces) of fruit, to which is added 125 gm. (about 4½ fluid ounces) of hot 17° Brix sugar sirup. The cans are vacuum closed and processed at 176° for 14 minutes.

The separated sections are extremely fragile, and much agitation or vigorous stirring will cause breakage. Washing and handling must be done with large volumes of gentle currents of water. A whirlpool floatation type of separator is best for washing and removing small fragments of membrane and peel. Much flavor is removed with all this manipulation, but the pieces are attractive in appearance.

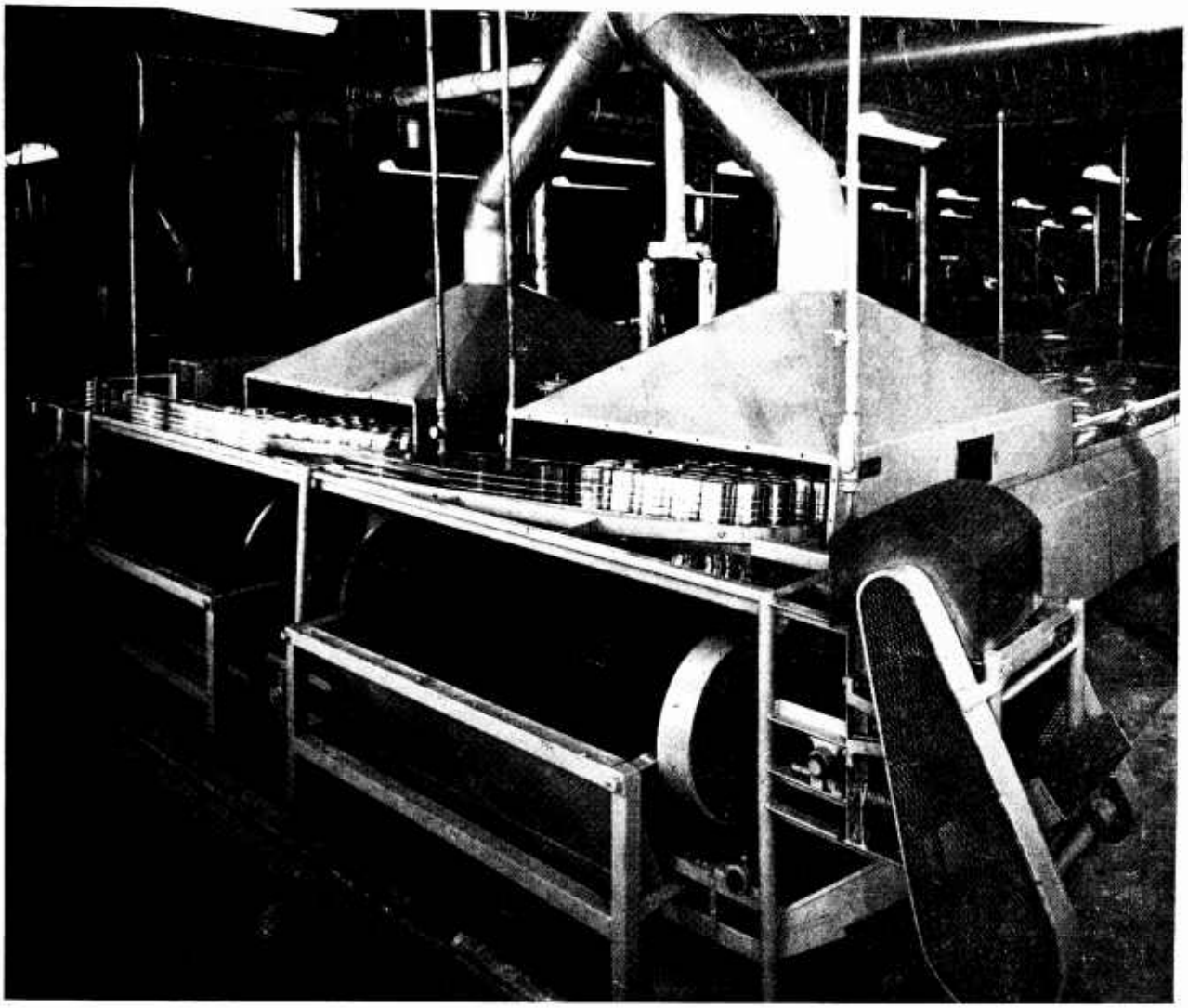


FIGURE 10.—Part of a cooker-cooler used in the processing of grapefruit sections. (Courtesy of American Machinery Corp., Orlando, Fla.)

Chilled Orange Juice

Although most citrus juices consumed in this country are preserved in one form or another by pasteurization, concentration, or freezing, considerable quantities of orange juice are distributed in California and in the Middle Atlantic and Northeastern States in the form of chilled single-strength juice. The juice may be packaged in milk bottles or waxed cartons, and shipped up to distances of 1,200 miles in refrigerated trucks.

Carload lots of unpasteurized orange juice, packed in 1-gallon hermetically sealed tin cans refrigerated with ice and salt, have been successfully shipped from southern California to New York City for distribution by dairies.

In Florida bulk shipments of orange juice are made in stainless-steel refrigerated tank trucks lined with plastic or glass (*486*). Sometimes the juice may be shipped in 1-quart waxed cartons. Most of the orange juice is purchased by hotels, hospitals, restaurants, and dairies. In Florida reconstituted frozen concentrate may be added to standardize the product or used to supply the market when suitable fresh fruit is not available for juicing. Sometimes the juice is given a heat treatment to improve cloud stability and otherwise extend storage life. In large cities this type of juice may be produced in small processing plants and distributed locally through juice bars, grocery stores, and dairies.

Chilled orange juice must compete with single-strength canned citrus juices, frozen

concentrates, and fresh fruit itself. The main advantage of the chilled juice is one of convenience, in that it enables restaurants, hotels, hospitals, and other large users to prepare this food easily for their customers. Many families are interested in the convenience of having high-quality orange juice delivered to their doorsteps.

Strict sanitary control of all procedures, from selection of fruit through processing and shipping, is necessary to insure superior quality of the product. The fruit should be thoroughly washed with a good detergent, rinsed, and dried. Cutting and reaming the fruit should be carefully controlled to maintain oil content of the juice at a low level. Heavy solid particles and seeds are screened out. If the juice is to be stored for more than 3 to 4 days, it should be deaerated to remove dissolved oxygen, which hastens flavor deterioration. The extracted and screened juice should be chilled as quickly as possible to 30°-32° F., preferably through a heat exchanger, filled into bottles or cartons with a minimum of head space, and tightly sealed. The juice should be kept at around 30° until consumed in order to preserve maximum quality. This temperature is lower than that generally maintained in most commercial and household refrigerators. Orange juice, because of its sugar content, will not freeze at this temperature.

Orange juice prepared by this method will retain most of its flavor and practically all its vitamin C content for storage periods up to 10-14 days when kept at the recommended refrigeration temperatures. During this period the microbial population of the juice usually tends to decrease.

Sulfured Citrus Juices

Sulfur dioxide is widely used for the preservation of citrus juices in the Mediterranean countries and in England. Its use in the United States is limited, because foods containing sulfur dioxide are not permitted under the pure-food regulations of certain States. Anyone planning to use this preservative in citrus juices for sale should consult applicable regulations for complete details.

The use of sulfur dioxide as a food preservative has been subject to regulation since the 15th century. The preservation of citrus juices with sulfur dioxide began to assume importance early in the 20th century, when Great Britain imported lime juice for use as a part of the official ration in its Navy, with a view to the prevention of scurvy. After the introduction of lime juice preserved with sulfur dioxide, lemon and orange juices and then grapefruit juice so preserved were imported for use in the preparation of beverages (also see p. 37). Sulfur dioxide is also used to preserve sliced and cooked citrus fruits for use in marmalade manufacture. In recent years it has been used extensively for the preservation of concentrated orange juice in bulk. In the citrus areas bordering the Mediterranean there are few processing plants with modern equipment for canning, concentrating, or freezing citrus juices; therefore, much of the processed juice is preserved with sulfur dioxide.

Sulfur dioxide is more effective against mold spores and bacteria than against yeast. It inhibits darkening and helps in reducing losses of vitamin C. However, it does not affect pectic enzymes, which are responsible for breakdown of tissue or which cause loss of cloud in citrus juices. Also, sulfur dioxide cannot be considered to have a permanent preservative effect in foods stored under conditions permitting reinfection. Being a gas, it tends to escape during storage in nonhermetically sealed containers, and it is quite likely that some of the sulfite is lost by reduction to sulfate. It also reacts with some of the constituents of fruit, notably aldehydes, ketones, and sugars, to form compounds lacking in preserving power. Since high temperatures accelerate both these actions, it is advisable to store sulfur dioxide-preserved foods in cool places.

Downer (*98*) states that the preservative effect of sulfur dioxide in acid juices is due to the undissociated sulfurous acid molecule. The effectiveness of sulfur dioxide as a preservative is a function of juice acidity, as a large concentration of hydrogen ions is necessary to repress ionization and permit the existence of appreciable numbers of sulfurous acid molecules. Although some investigators report that sulfur dioxide exerts a very slight destructive effect on vitamin C in citrus juices, Hamburger and Joslyn (*143*) found no evidence of such action. Apparently sulfur dioxide competes with the vitamin for any free oxygen present and therefore inhibits rapid early oxidation of the vitamin. The final minimum value of vitamin C is independent of the presence or concentration of sulfur dioxide.

The amount of sulfur dioxide required depends on the acidity (pH) of the juice and the amount of suspended pulp. Clarified lime juice can be preserved safely with as little as 350 p. p. m., but pulpy orange juice requires as much as 1,500 p. p. m. (0.15 percent). Thorough mixing of preservative with juice is essential, as an unprotected pocket may begin to ferment, after which no amount of preservative will prevent the loss of the entire contents of the container.

Aging or subjecting citrus products to elevated temperatures accelerates the inversion of sugars, with an increase in aldehyde (glucose) content. Therefore, products so treated require larger amounts of sulfur dioxide for adequate preservation. Cooked pulps for marmalade are usually treated with 2,000 p. p. m. or more of sulfur dioxide. When sulfur dioxide is used to preserve concentrated orange juice, 2,000 to 2,500 p. p. m. must be added to give a residual-free sulfur dioxide sufficiently high to prevent infection for any appreciable storage period. Although combined sulfur dioxide does not exert preservative effect, it does affect flavor. Excessive amounts will also cause bleaching. It is desirable, therefore, to avoid such high dosages wherever possible. Ingram (*200*) recommends that orange concentrate be heat processed and hermetically sealed until ready for use. It may then be treated with sufficient sulfur dioxide to counteract any contamination picked up during repackaging or subsequent processing. Where infection may occur at several stages, the best plan would seem to be to handle at low temperature to minimize the activities of micro-organisms and to add sulfur dioxide as late in the process as possible (*200*).

For large-scale operations the most economical way to apply sulfur dioxide is as the pure gas. This is accomplished by placing the cylinder containing sulfur dioxide on a scale so that loss of weight can be measured. A copper tube is connected to the valve of the cylinder and extended into the juice to be sulfured. Care should be taken to see that no iron comes in contact with the juice, as it will cause discoloration in the sulfured product. The operation should be carried out in a well-ventilated room, because there is always escape of some gas, which is extremely irritating to mucous membranes. Gas should be bubbled slowly through the juice to assure complete absorption.

Another way of adding sulfur dioxide is by means of water solutions of a sulfite salt. The following method will be found satisfactory. Place a strip of adhesive tape at the 5-gallon level of a 5-gallon bottle of water. Pour out 1 gallon into a bucket. To the bottle add *one* of the following: (1) 10 pounds of sodium metabisulfite (theoretically 64 percent of sulfur dioxide), (2) 10½ pounds of sodium bisulfite (theoretically 61.5 percent of sulfur dioxide), or (3) 12 pounds and 5 ounces of potassium metabisulfite (theoretically 57.6 percent of sulfur dioxide). Shake until dissolved and pour back the water from the bucket until the 5-gallon mark is reached. The mixture thus obtained is a stock solution and should be maintained tightly stoppered. Each fluid ounce of this solution will contain 0.01 ounce of sulfur dioxide.

As an example of its use, suppose it is desired to add 800 p. p. m. of sulfur dioxide to a barrel of juice. Put 1 quart of the solution and 400 pounds of juice into the barrel. The next day, after foam has settled, nearly fill the barrel with juice and determine the net weight. This will be found to be between 444 and 475 pounds. Subtract 400 pounds from the net weight, and for every 12.5 pounds over 400 pounds add 1 fluid ounce of stock solution. For example, if the net weight is 457 pounds, subtract 400 pounds. Then the difference, or 57, is divided by 12.5, which gives 4.56. Therefore, add 4.6 ounces more of the stock solution. This will give a final concentration of 800 p. p. m. of sulfur dioxide.

Pasteurized Concentrates

In general, the process used commercially for the manufacture of pasteurized concentrates is essentially the same as that used for frozen concentrates (p. 38), except that the former are heated sufficiently to completely inactivate pectic enzymes and to destroy spoilage organisms. This is necessary, since these concentrates are generally intended for storage at temperatures above freezing (usually at about 40° F.).

Procedures for washing, sorting, sizing, and inspecting the fruit and extracting and finishing the juice are the same as those used in the preparation of other citrus products. If the concentrate is to be used for the manufacture of compounded products, the fruit may have a wider range of soluble solids-acid ratios than that intended for single-strength or frozen concentrates, since these juice variables will be adjusted in the final product. If the concentrate is to be used as a pure-juice beverage, the usual precautions must be observed in controlling these fruit qualities (*253; 435, pp. 677-695*).

The juice is evaporated to the desired concentration in a vacuum evaporator. Older types of evaporators operate at 120° F. in the optimum temperature range for enzymes present. To prevent enzymatic deterioration during evaporation, the juice is heated to 190°-200° just before it enters the evaporators. Newer falling-film, low-temperature evaporators operate at about 70°, and it is not essential that a preliminary heating be conducted. In either case the concentrate is heated and filled hot into cans to prevent spoilage.

As discussed under pasteurization (p. 27), single-strength juice must be heated to approximately 200° F. to prevent cloud loss. If

the heat treatment is performed on the concentrate, there is reported evidence (*219*), generally known to the industry, that less heating time is required to inactivate pectic enzymes than is necessary for single-strength juice.

Heat treatment is directed not only toward inactivation of pectic enzymes to prevent cloud loss but also toward destruction of spoilage micro-organisms. A common practice is to flash-heat the single-strength juice as it is fed to the evaporator, and if the concentrate is to be preserved in cans, it is reheated to approximately 170° F., filled hot into cans, hermetically sealed, and cooled. Another practice is to prepare an unheated concentrate, fill into oak barrels or steel drums lined with polyethylene bags, and hold in frozen storage. When needed, the product is thawed, flash pasteurized, and packaged as required.

Concentration of citrus juices is carried out in either of two general types of vacuum evaporators (*435, pp. 677-695*). One is a low-temperature, falling-film type, which operates in a temperature range of 60° to 80° F. (p. 40). The other is the conventional type, which operates in a temperature range of 100° to 120°. This type is now nearly obsolete, because the product obtained cannot compete in quality with that prepared in the falling-film type of evaporator.

The two types of concentrates are generally used for different purposes. The product produced at the higher temperatures is used exclusively in beverage bases, condiments, and candies. The low-temperature product, being superior in flavor, is marketed as a concentrated pure-fruit juice in addition to these other uses. The low-temperature process is gradually becoming the principal method for manufacturing citrus concentrates intended for room or cool storage.

A wide range of concentrated citrus juices is produced, the degree of concentration depending on the ultimate use. Concentrated orange juice packaged in No. 10 cans, gallon cans, or paraffined barrels for bulk handling is commonly of 60° to 70° Brix, although higher concentrations are available for special use. The degree of concentration of grapefruit juice is generally lower than that for orange juice (*253*). Highly concentrated grapefruit juice tends to brown during storage, the degree of browning being in direct proportion to the degree of concentration.

Concentrated citrus juices should be stored at temperatures of 35° to 40° F. to prevent development of off-flavors and browning. Studies on the storage deterioration of pasteurized concentrated orange juice indicate no significant effect of degree of concentration (13°-71° Brix) at either 40° or 60° F. on development of off-flavors. At 80° and above a marked change in flavor occurs with increase in concentration (*81*). No significant browning is noted in concentrates held 1 year at 40°. At 60° and 80° darkening increases as concentration increases (*81, 84*).

Other types of spoilage may occur in canned concentrated orange juice. Cans of concentrate stored at room temperature develop swells either by chemical decomposition or by yeast fermentation (*68*). Gas formation is caused by fermentation on storage at 80° and 95° F., but not at 40° or 120° (*82, 84*).

There are United States standards for grades of concentrated orange juice for manufacturing (*443*) and tentative grades for canned concentrated grapefruit juice (*439*).

In the preparation of pasteurized concentrated lemon juice, single-strength juice is pasteurized at approximately 175° F. to stabilize the cloud and destroy micro-organisms before it goes to the evaporator. Concentration is carried out in low-temperature, falling-film evaporators and conventional vacuum pans. Low temperatures are especially desirable for lemon juice to prevent browning during evaporation. Numerous variations are practiced in concentrating lemon juice. The heated juice may be fed directly to the evaporator and flash cooled, or it may be cooled in a separate heat exchanger and fed to the evaporator as needed. After the juice is concentrated, it is filled into barrels and stored at 40°. This product is used almost exclusively in the bottling trade for soft drinks.

In the preparation of a concentrate for lemonade, single-strength lemon juice is mixed with concentrated juice, pumped through a deoiler, and then rapidly cooled to 50° F. It is then pumped to a tank, where dry sugar is added to bring the concentration to approximately 50° Brix. This siruplike concentrate is heated to approximately 160° F., filled into cans, sealed, and cooled. The concentrate is generally stored at 40°.

Beverage Bases

Beverage bases have been manufactured for many years by citrus-fruit processors. The popularity of these products has been based on the wide acceptance of carbonated fruit-base drinks (soda pop). Orange has proved the most popular and is the most widely used for all fruit concentrates for beverage purposes. These fruit concentrates have a wide variety of uses in the preparation of beverages and foods.

BOTTLER'S BASE FOR CARBONATED DRINKS

Juice for bottler's base, which should be low in peel extractives, is pasteurized at 200° F. for about 4 seconds to inactivate pectic enzymes and stabilize the juice cloud, which is essential to achieving a cloudy, fruitlike appearance in the final carbonated drink. The pasteurized juice is concentrated under vacuum at about 110° F. to 65° Brix. The concentrate thus obtained is mixed in a refrigerated tank with the desired amount of sugar, citric acid, citrus oil, brominated olive oil to prevent separation, certified food coloring, and benzoate of soda; homogenized; again pasteurized at 170° F. (125° if benzoated); filled hot into gallon-size citrus enamel cans; and hermetically sealed. These products should be stored at 55° to 60° for preservation of their flavor and to prevent browning. One gallon of such a base makes from 20 to 100 gallons of citrus beverage when mixed with carbonated water (*192, 433*). Carbonated citrus beverages contain approximately 6 percent of actual fruit juice. Their composition is given in table 17.

TABLE 17.—*Average composition of citrus-flavored carbonated beverages* (433)

Flavor	Samples	Sugar	Gas volume[1]	Citric acid	pH
	Number	*° Brix*	*Units*	*Gm. per liter*	
Lemon	348	11.18	3.2	1.20	3.07
Lemon and lime	20	11.04	3.2	1.75	3.01
Lime	54	11.10	3.7	2.28	2.90
Lime, lithia	54	9.17	4.0	1.40	3.02

[1] Unit volumes of gas dissolved in each unit volume of the beverage.

PASTEURIZED BASE FOR NONCARBONATED DRINKS

This product, often called a beverage concentrate, is a mixture of natural juice with sugar sirup, acidified with citric or tartaric acid, flavored with citrus oils, and colored with certified food colors. Some of the better grades are acidified with lemon or lime juice. The mixture is deaerated, flash pasteurized to stabilize the juice cloud and prevent fermentation, and filled into citrus enamel cans, which are sealed and cooled immediately. To prepare the finished beverage, generally 1 part of the concentrate is mixed with 5 parts of water.

BEVERAGE BASES PRESERVED WITH SULFUR DIOXIDE

There has been an export market, particularly to England, for a limited amount of bases for use in the preparation of beverages, such as orangeade, lemonade, limeade, squashes, and variously flavored barley water. The beverage base is diluted with water, sweetened, acidified, and flavored to suit the trade to which the bottler is catering.

The trade calls for three types of products—"clear juice," "green juice," and "whole fruit with top oil" (see also p. 29). Clear juice is made by pressing the cleaned fruit through a screw press, screening, and separating the undissolved oil. The resulting liquid is treated with 1,200 p. p. m. of sulfur dioxide and allowed to stand until the clear juice can be siphoned or decanted off. On analysis the product will show about 800 to 900 p. p. m. of sulfur dioxide as a result of handling, and this amount will be further reduced by the time it reaches the bottler.

Green juice, or pulp juice, usually consists of the material obtained by passing peeled fruit through a screw press and then through a screen with 1/8-inch holes. It is a turbid product, and may be packed with added juice sacs if these are desired.

The whole fruit with top oil is similar to the green juice, except that the fruit is not peeled, or is only partly peeled, before it is passed through the screw press. It contains the full amount of juice sacs and some peel and oil.

These bases are usually packed in paraffined white oak barrels or in steel drums lined with polyethylene bags, and preserved with approximately 1,200 p. p. m. of sulfur dioxide.

Citrus beverages prepared from bases as described are poor sources of vitamin C, or ascorbic acid (table 18), as compared to canned single-strength juice or reconstituted frozen concentrate. They lose their vitamin C content

TABLE 18.—*Analysis of citrus-juice beverages* [1]

Producer	Contains juice of—	Soluble solids	Citric acid	Brix-acid ratio	Ascorbic acid
		° Brix	*Percent*		*Mg. per 100 ml.*
A	Orange	13.4	0.31	43.2	1.42
B	Orange	12.8	.77	16.6	27.8
	Tangerine	15.2	.72	21.2	14.8
C	Orange	13.1	.96	13.7	38.2
	Grapefruit	11.3	1.03	11.0	16.5
D	Orange	13.2	.53	24.9	12.1
	Grapefruit	11.7	.48	24.4	3.56
E	Orange	10.8	.35	30.8	1.95
F			.15		0
G	Orange	14.0	.24	58.3	.89
H	Lemon [2]	10.4	.32	32.5	.36
	Orange [2]	15.7	.10	157.0	0

[1] Condensed from Roberts (*361*).
[2] Carbonated.

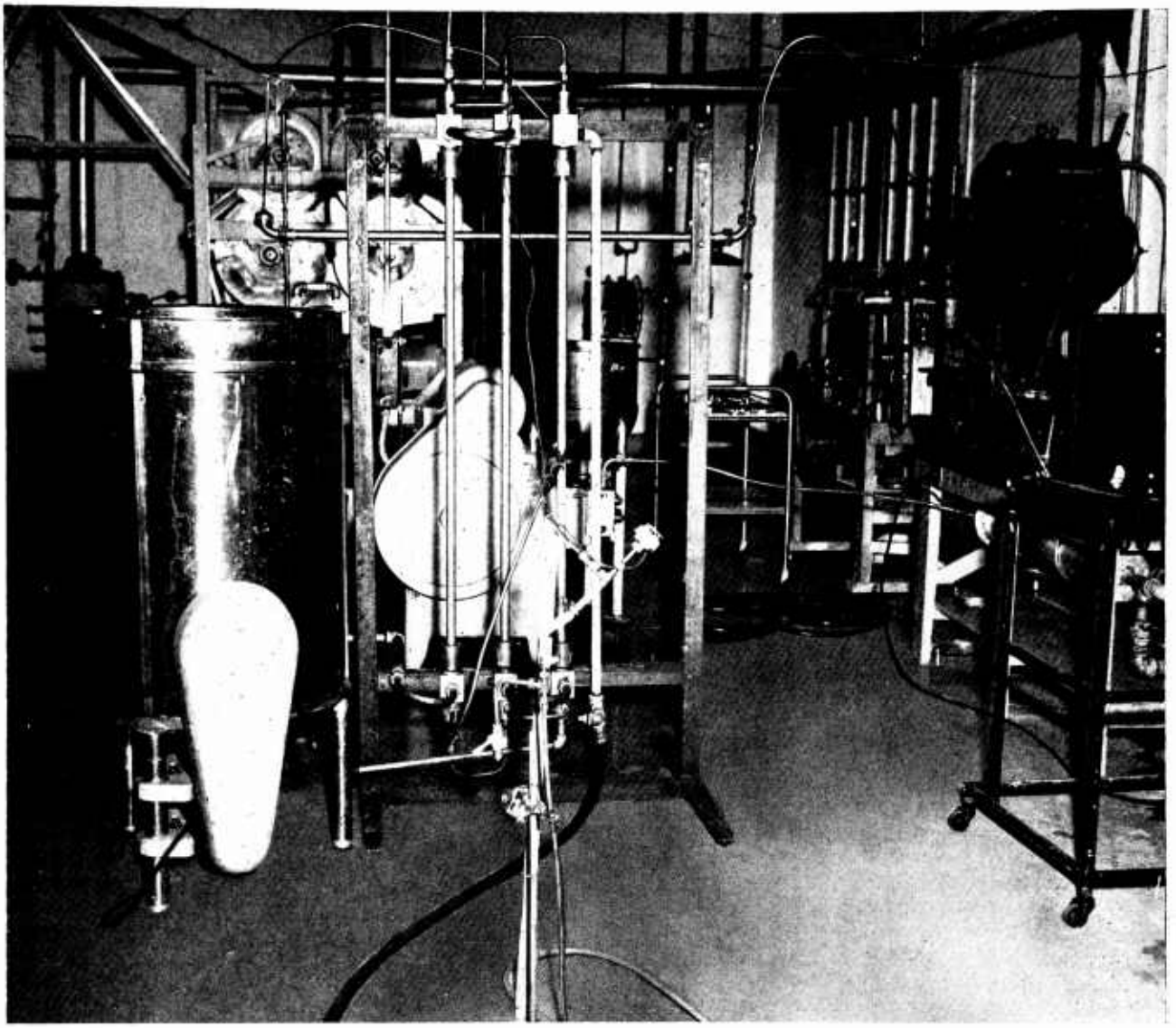


FIGURE 11.—Part of the pilot plant at the Citrus Products Station (U. S. Dept. Agr.) at Winter Haven, Fla.

rather rapidly, losses varying from 7 percent to nearly 70 percent in a week's time depending on the product (*361*). Investigations in this field have been reported elsewhere (*62, 265*).

Frozen Concentrates

FROZEN CONCENTRATED ORANGE JUICE

Frozen concentrated orange juice was the first citrus product of its type to be produced in large commercial quantities, and continues to be the leader among frozen juice concentrates. Its development has been so spectacular that it has been the subject of several feature stories in popular magazines and of many reports in trade and technical journals. Production began in the 1945-46 season, and increased steadily until over half the Florida orange crop is used for frozen concentrate.

The development of frozen concentrated orange juice came about as a result of a definite need. Pasteurized concentrated orange juice (p. 35) had been used for some time in beverage bases and candies, but only limited quantities were reconstituted into single-strength juice and used as such. This product suffered in flavor during manufacture and would deteriorate rapidly in storage (*81*). Frozen single-strength orange juice has been marketed on a limited scale, and showed good retention of quality in storage, much better than the canned product held in common storage. However, it did not strike popular fancy,

possibly because it freezes solid and requires time to defrost.

Early in 1944 investigations were begun at the Citrus Products Station of the United States Department of Agriculture, Winter Haven, Fla. (fig. 11), in cooperation with the Florida Citrus Commission, on methods of improving the quality of concentrated orange juice. It was found that the usual temperature (120° F.) at which vacuum evaporators were operated resulted in flavor damage during concentration, and that this damage was largely eliminated if the temperature during evaporation was lowered to 60°-80°. Even though no off-flavors were formed, the product still lacked the flavor of fresh juice when reconstituted. Volatile fractions, especially peel oils, contributing to the aroma and flavor were largely lost during concentration.

It was found that the addition of a small portion of fresh juice [5] would restore sufficient natural flavor so that the reconstituted juice resembled fresh juice rather closely. Attempts to recover volatile constituents lost during evaporation and return them to the concentrate instead of adding fresh juice to enhance the flavor have not been successful (*301*). The use of carefully selected cold-pressed orange oil has been shown to restore the volatile flavor and aroma lost during concentration of California orange juice (*354*).

A patent (*263*) covering the use of low temperature during evaporation and the addition of fresh juice to the concentrate for the enhancement of flavor was granted and assigned to the Secretary of Agriculture of the United States. In the process developed evaporation was continued until a concentrate of 55° to 65° Brix was obtained, then fresh juice was added

[5] First suggested by L. G. MacDowell, director of research of the Florida Citrus Commission.

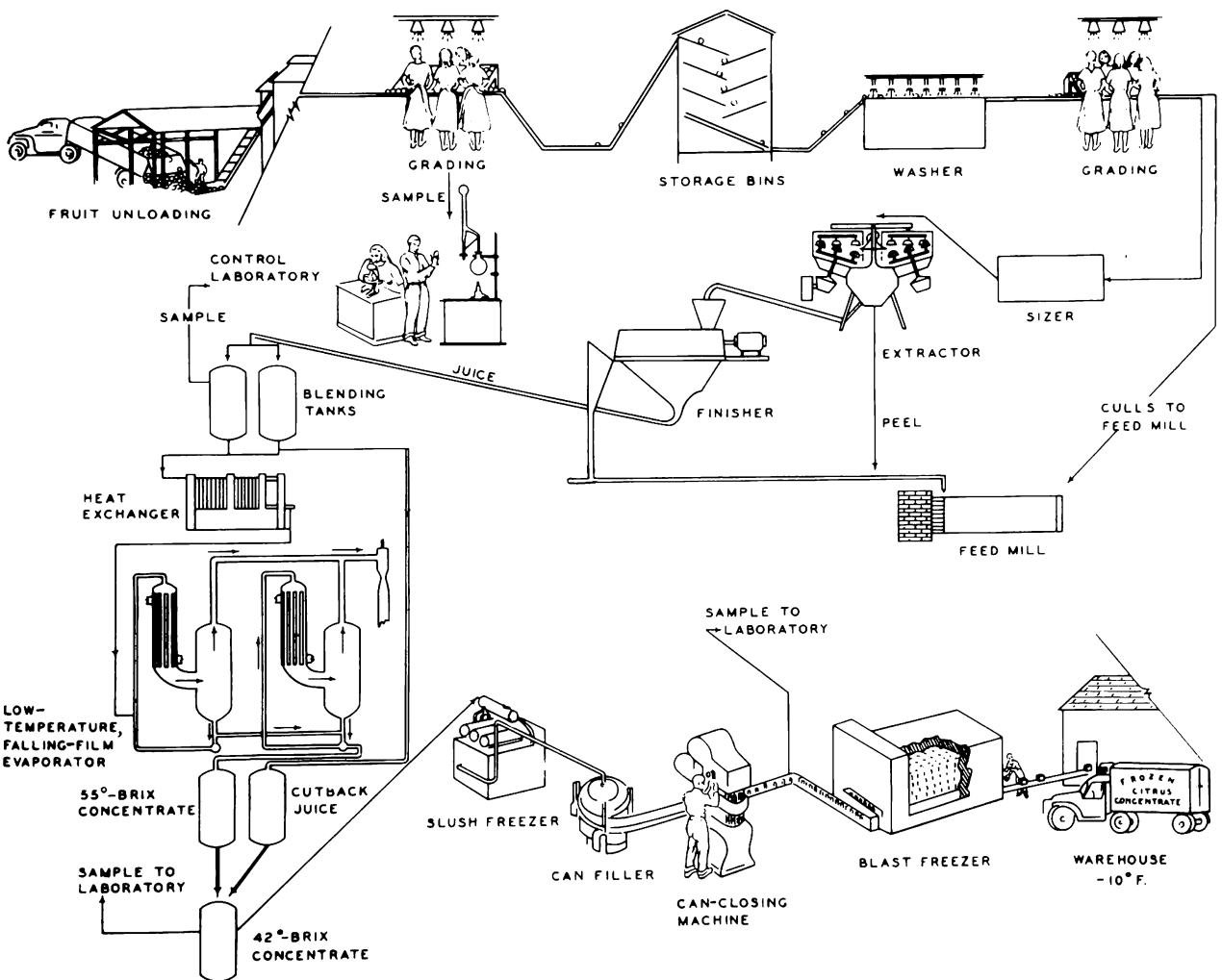


FIGURE 12.—Flowsheet showing steps in the production of frozen concentrated orange juice.

until the concentration was reduced to 42° (± ½°). The fresh juice added, called "cutback" in the industry, amounted to 7-10 percent of the total juice used.

At 0° F. the 42°-Brix concentrate is not frozen solid, but contains considerable ice and is rather stiff. The heat in the water required for reconstitution is sufficient to melt the ice, and the melting ice absorbs enough heat to assure a cool drink. Reconstitution is accomplished by adding 3 cans of water to 1 can of concentrate, which makes a product of 11.7° to 12° Brix.

Many of the steps in the production of frozen concentrated orange juice (fig. 12) are the same as those in the production of canned single-strength citrus juices (p. 24). Fruit is usually received at the plant in bulk in large trucks holding up to 36,000 pounds. The trucks are tilted or backed into pits so the fruit flows out by gravity onto conveyors, where broken, bruised, or otherwise unsatisfactory fruit is removed. The fruit is elevated into bins where it is held until needed, because a limited amount of storage is necessary for the 24-hour-per-day operation. It is processed as soon after harvest as possible, usually within 24 hours. Fruit from different bins, which has been previously analyzed for soluble solids and acid, is mixed in order to give a more uniform product. The fruit is first immersed in water or sprayed to wet it and to remove loose particles. Then a detergent is applied while the fruit passes over continuously rotating nylon or bristle brushes. A water rinse follows, and then a germicide is applied. Water with 12 to 50 p. p. m. of chlorine may be used, or a 250-p. p. m. quaternary ammonium compound solution may be applied as a fine mist, to be removed by rinsing just before the fruit goes to the extractors (*27, 43*).

Extractors are the same as those used in the preparation of juice for canning. The juice passes from the extractors to the finishers, where pulp, seeds, and rag are removed. Two cylindrical, screw-type finishers are commonly used in series. The first finisher has a fine screen with about 0.020-inch perforations. The juice from this machine is comparatively free of coarse pulp and passes to the evaporator. The pulp from the first finisher, along with some juice, passes to the second finisher, which is fitted with a screen having 1/16-inch to 1/8-inch perforations. This juice is comparatively high in coarse pulp particles and is used as cutback. The cell fragments make the reconstituted concentrate resemble fresh juice in appearance as well as in flavor.

In some plants juice passes directly from the finisher to the evaporator, whereas in other plants it goes to holding tanks of about 1,000-gallon capacity. If holding tanks are used, they are of the coldwall type, where the juice is cooled to about 40° F. Use of holding tanks permits analyses to be made for solids and acid as a check on the efficiency of mixing fruit from the bins to produce juice of desired soluble solids-acid ratio.

Evaporators are of various types, but all have several features in common and accomplish approximately the same results (*381*). All make use of falling-film heat exchangers, in which the juice runs in a thin film down the inside of a tube while the tube is gently heated from the outside. Since the film of juice is thin, local overheating is prevented. Another advantage is that the heat-exchange rate is high and the temperature of the heating medium can be kept low, so that the chance of overheating is further decreased.

The temperature of the juice during evaporation depends on the design of the unit, but is kept in the range of 60° to 80° F. In order to accomplish evaporation at these temperatures, evaporators of advanced engineering design have been developed (fig. 13). All reuse energy in one way or another. Some use the hot side of ammonia compressors to provide heat to evaporate water from the juice and the cold side to condense the vapors (*2, 74, 164, 220*) ; others use large steam boosters or thermocompressors to raise the temperature of the vapors coming from the juice in one stage so that they can be used to furnish the heat required for evaporation in the next stage (*12, 13*). Stainless steel is the standard material of construction for all parts coming in contact with the juice or concentrate.

The juice is concentrated to 55° to 63° Brix, depending on the policy of the manufacturer or the specifications of the purchaser. Evaporators operate in a continuous manner, with fresh juice being added at one point in the system and concentrate being constantly removed at another. The evaporators operate in 2 or more stages, 4 and 6 being quite common, concentration being carried to a predetermined point in each stage, and the partially concentrated juice then passing to the next stage, where more water is removed, and so on until the desired concentration is reached. These stages generally operate with a common vacuum source and at about the same temperature. Some units operate as two or more effects, with the vapors from one effect providing the heat of vaporization for the next, and thus save fuel (*220*). The volume of juice is held at a minimum in each stage, so that the total time required for evaporation is 20 minutes or less.

The concentrate is collected in a coldwall

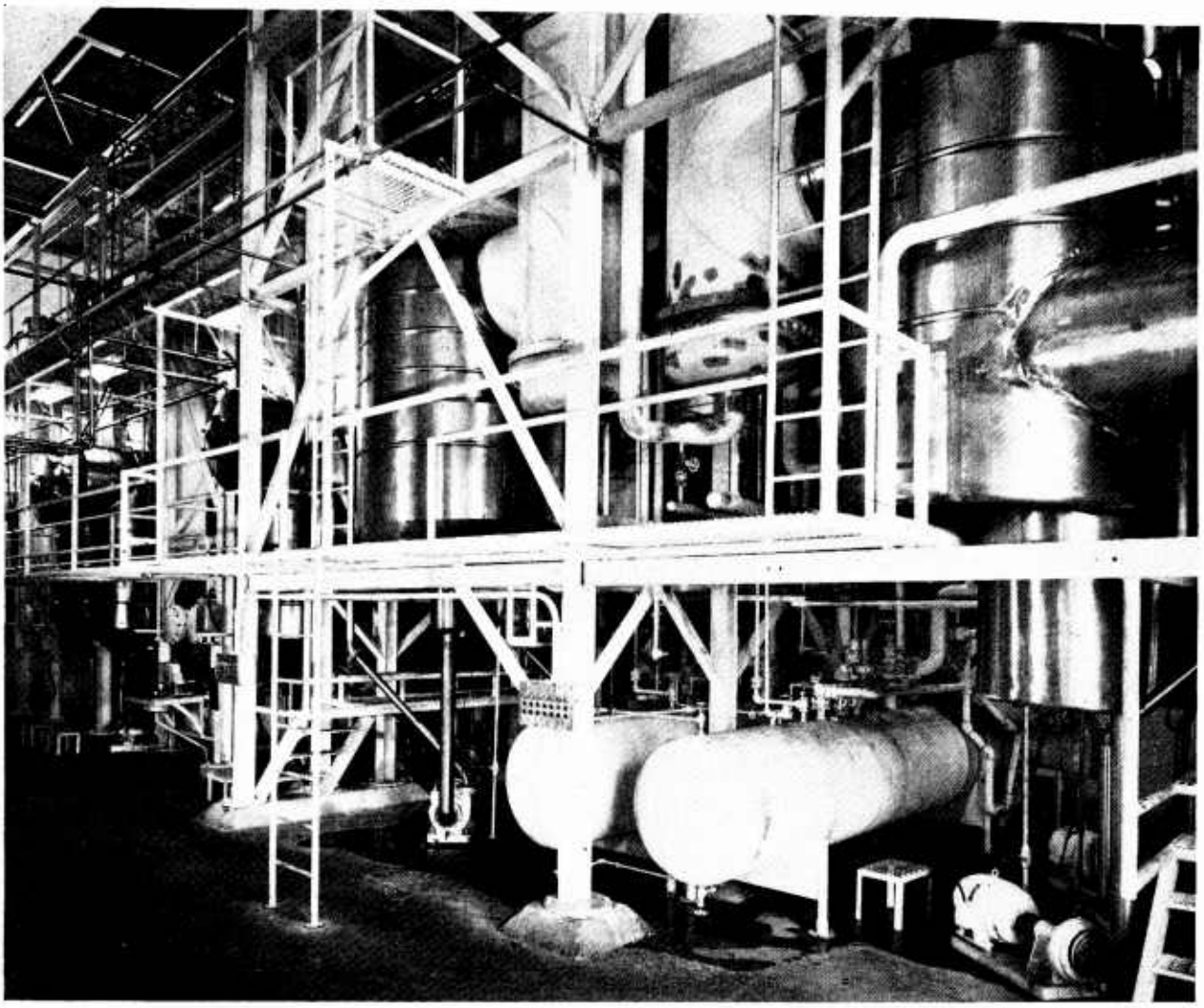


FIGURE 13.—Battery of evaporators for concentrating orange juice in the preparation of frozen concentrate. (Courtesy of Florida Citrus Canners Coop., Lake Wales, Fla.)

tank, where the temperature is held at 35° F. or below, and here its concentration is determined by a refractometer and expressed as degrees Brix, corrections being made for temperature and citric acid content (*413*). Cutback juice is then added until a concentration of 42° Brix (± ½°) is attained. If the oil content is below the desired level (0.025 ml. per 100-gm. concentrate), cold-pressed orange oil may be added, care being taken to agitate the concentrate sufficiently to insure even distribution. When the adjustments have been made for concentration, peel-oil content, and acidity, the concentrate is further cooled in the coldwall tank or a continuous cooler (fig. 14) to about 20° to 25° F.

Because 42°-Brix concentrate is rather thick and begins to freeze at about 18° F., piston-type fillers with positive action are used to handle the viscous product. Steam is injected beneath the lid of the can before sealing to sweep out the air in the head space and sterilize the lid. When the steam condenses, a vacuum is developed in the can.

Final freezing may be done while the cans are conveyed on a perforated belt in an air blast at —40° F. (fig. 15), or the cans may be frozen by immersion in a refrigerated denatured alcohol-water mixture; agitation and liquid contact promote rapid freezing. After the product has been frozen, it is stored in a refrigerated warehouse at 0° or below. Similar temperatures are maintained during transportation and distribution.

To produce a uniform product it has been found desirable at times to save the concentrate

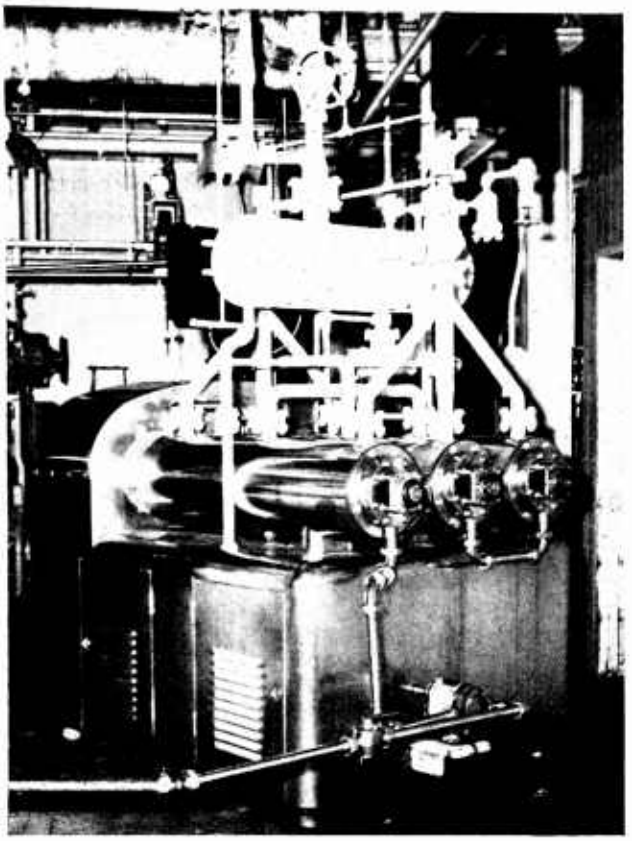


FIGURE 14.—Continuous slush freezer for chilling concentrated citrus juices before canning and freezing.

from one part of the season for use when the solids-acid ratio of available fruit is either too high or too low to prepare a concentrate of the desired quality. A concentrate stored for such purpose has come to be known in the industry as "addback." Sometimes addback may come from a different producing area. A concentrate of 55° to 63° Brix is filled into bulk containers (5 to 55 gallons) lined with polyethylene bags and placed in frozen storage. When needed, the concentrate is brought out, thawed, and mixed with fresh concentrate along with the cutback juice.

Concentration by Freezing

Concentration by freezing has attracted the attention of engineers for some 35 years, and as long ago as 1914 Gore concentrated cider by this method (*132*). The process is interesting because no heat is applied, which might affect the delicate flavor, and theoretically less energy transfer takes place in freezing than in evaporating water. Considerable effort has been made to develop this method on pilot-plant and full-plant scale, but commercial operations have been limited. Sufficient material has been processed and tested in market surveys to indicate that an acceptable product can be produced in this way.

However, several difficulties have been encountered in commercial application of the method, and some of the expected advantages over vacuum evaporation have not been realized. Much of the suspended matter and soluble solids remain in the ice and leave the concentrate light in color and low in characteristic orange flavor. Large crystals facilitate separation of the ice, but such crystals form slowly and much of the product needs to be held in the processing operation. The degree of concentration that can be attained in a single freezing and centrifuging is limited, but it can be further increased by freezing the concentrate and centrifuging again. Usually two freezings are necessary to obtain a concentrate of 45° Brix. The ice from the second freezing needs to be reworked in order to avoid excessive loss of soluble solids. Flavor and texture can be restored with pulpy cutback, but the amount that can be used is severely limited by the impracticability of overconcentrating, as in the case of vacuum concentration.

Most of the work has involved freezing in containers immersed in refrigerated brine (*408*), but the application of high vacuum to induce rapid evaporation to cool and freeze has also been tried. A "step-freeze" process (*246*) has been developed, in which freezing occurs rapidly, and the product is conducted automatically from one stage to the next.

Quality Control

Control of quality during the manufacture of frozen concentrated orange juice is most important, and beginning with the selection of fruit it continues through all operations. Care must be taken to see that fruit of proper maturity is being purchased to satisfy the requirements of grade standards and any special standards of the processor or purchaser. The usual tests for maturity include determination of soluble solids and citric acid and calculation of the Brix-acid ratio. Current United States standards for fancy, unsweetened, frozen concentrated orange juice specify that this ratio must be not less than 11.5:1 nor more than 18:1; these standards also specify a minimum and maximum citric acid content (*441*). In Florida a State law prohibits the addition of sugar to this product, and therefore the fruit must produce a concentrate within the above ranges to receive this grade. Fruit is sometimes purchased on the basis of soluble-solids content, because juice of higher soluble solids requires less evaporation of water to reach the desired concentration, and manufacturing costs are reduced. In addition to reduction of such

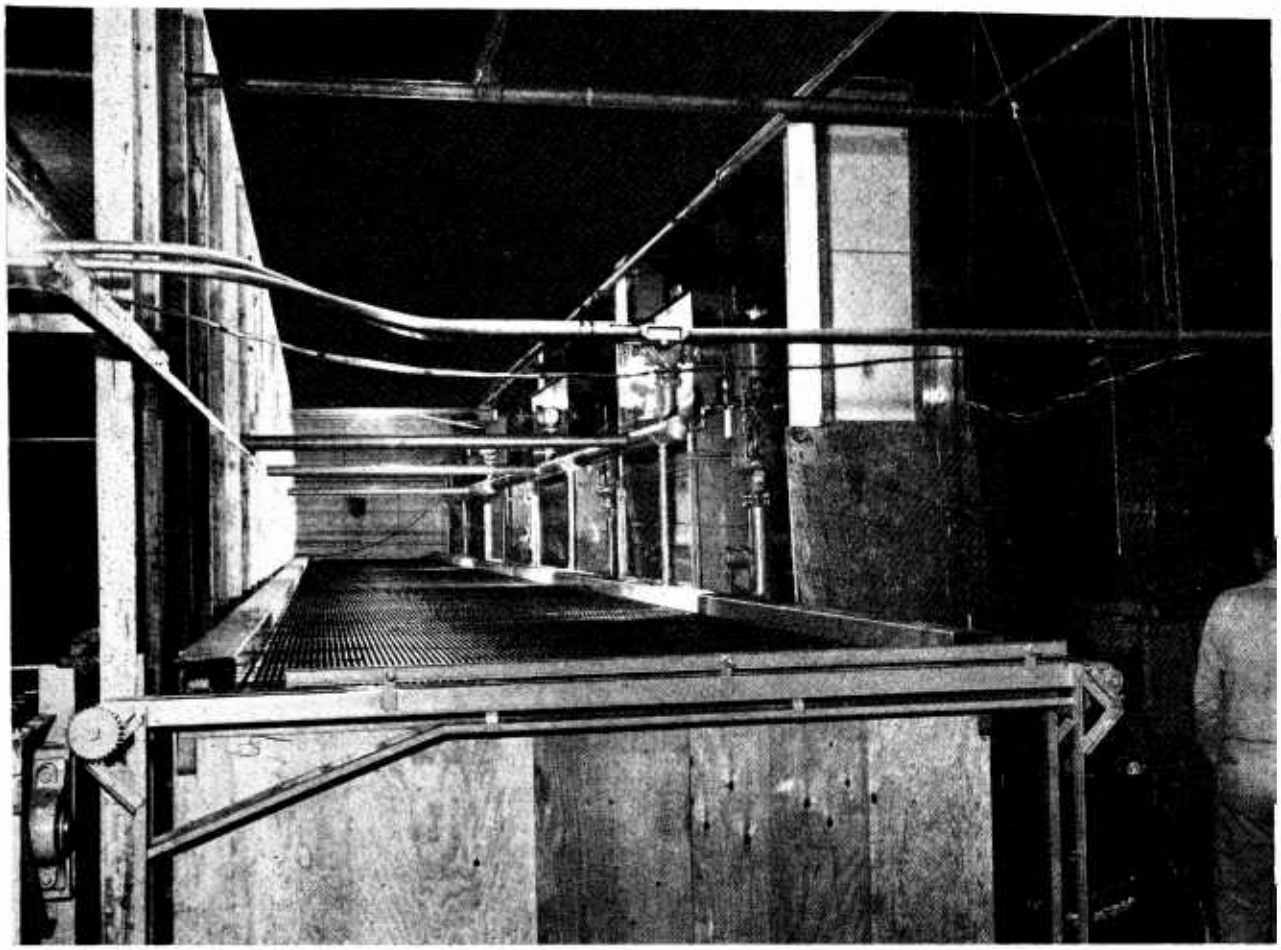


FIGURE 15.—Air-blast freezing tunnel for freezing concentrated orange juice. (Courtesy of American Machinery Corp., Orlando, Fla.)

costs, a higher yield of concentrate is obtained from a given number of gallons of fresh juice (*470*).

Generally the field buyer has a good idea of the condition of the fruit, and often "grab samples" may be taken from the top of the load in the yard to check its suitability. A larger and more representative sample is automatically taken as the fruit is conveyed from the trucks to the storage bins. Solids and acid content and juice yields are determined. Advantage is taken of the information regarding the analysis of fruit in the bins in order to maintain by blending a Brix-acid ratio within as close limits as possible.

The next point of sampling is the blending tank, and here again there is opportunity to mix juices of high and low ratio.

Concentration at each stage of evaporation is checked periodically to see that the plant is operating properly. A Brix hydrometer is used to determine the soluble-solids content of fresh juice and a refractometer is used for concentrates. Special care is taken to check the Brix of the concentrate leaving the evaporator and after blending with the cutback juice. Samples for analysis of recoverable oil are taken after the cutback juice has been added. Oil levels are usually maintained at about 0.025 ml. per 100 gm. of concentrate. Maintaining such levels can be controlled to a large extent by the method of extraction of the cutback juice, and can be supplemented by the addition of cold-pressed orange oil. Further tests may be made to determine the tendency to clarify and the possibility of gel formation (*44*) during storage.

Sanitation is an important factor in quality control (*27, 43*) (see also p. 45). Great care must be taken to insure that the fruit carries a minimum number of organisms into the plant, that decayed or bruised fruit is removed at the inspection table, that equipment is kept clean and sanitary, and that micro-organisms are not allowed to develop in appreciable numbers at any stage during processing (*112, 469,*

479, 482, 483). A close check should be kept of the concentrate being produced, and microbial counts should be made regularly. The frequency of such checks depends on the size of the operation and specifications of the manufacturer, but several samples should be taken in each shift. Periodically surface counts should be made of the unwashed and washed fruit, conveyors, and belts to check the effectiveness of sanitary procedures in use.

Since agar-plate counts require 2 to 3 days before the number of colonies can be determined, this method has been supplemented by more rapid direct counts (*480*). Although these direct counts are not so accurate as plate counts, they provide an immediate check on plant conditions.

Organisms have been found that are capable of developing in the first stage of evaporation, and they cause disagreeable off-flavors (*113, 161, 162, 305*). At times the incidence of organisms of this type has been discovered by direct count or by detection of diacetyl (*182, 469*) before the numbers reached serious proportions.

Each plant establishes a regular cleanup schedule, based on experience in the plant and especially on results of routine bacteriological tests (*27, 43*). The schedule varies with the arrangement of the equipment and the condition of the fresh fruit, and is more frequent in warm weather than in cool.

Another problem associated with extended operation is the formation of a film of hesperidin (p. 61) on the tube surfaces of the falling-film evaporators. Not only does this film interfere with the rate of heat exchange (slowing the rate of production) but if allowed to form in sufficient thickness it will flake off and appear in the finished product as harmless but unsightly white scales. Formation of hesperidin scales has at times forced shutdowns and necessitated doubling the frequency of cleaning.

Cleaning an evaporator begins with washing with warm water to remove adhering concentrate, followed by treatment with warm, dilute caustic soda to remove hesperidin and other films, a thorough scrubbing by hand of any remaining unclean surfaces, and final rinsing with clean water. A detailed inspection is made to check the efficiency of the cleaning.

Juice extractors are cleaned more frequently, once each 8-hour shift or more often. Some plants have an extra row of extractors, and one row at a time may be out of service for cleaning. Most extractors are equipped with spray nozzles to enable rinsing with high-pressure, chlorinated-water sprays during brief periods while juicing is stopped. Belts and other conveyors are kept wet with chlorinated water to prevent growth of micro-organisms.

A frozen concentrate will maintain its quality during storage at 0° F. for a year or more. At 5° changes are slow but perceptible. At 10° or above the rate of change increases considerably, and if the concentrate is allowed to remain for long at this temperature, deterioration becomes significant (*101, 297*). The first evidence of deterioration is a loss in the amount of suspended matter or cloud. As deterioration proceeds the upper portion of the reconstituted juice will become completely clear in 5 to 10 minutes after mixing. The concentrate may also exhibit gelation in the can. This is noted first by a slight lumpiness or weak gel, but in extreme cases the concentrate will retain its form even after having been removed from the can (*365, 471*). Off-flavors also develop under conditions permitting these physical changes, but are not evident until clarification is well advanced.

As previously pointed out (p. 6) gelation and clarification are considered to be associated with the action of the enzyme pectinesterase. Methyl groups are split off from the pectin molecule to produce low-methoxyl pectin, which in turn reacts with normally occurring calcium or magnesium ions to form a gel. In concentrated orange juice favorable pH conditions exist for this type of gel formation.

If the product is kept at 0° F. or below, gelation and clarification do not take place. The rate of deterioration at higher temperatures depends on whether or not a heat treatment has been used, the variety of fruit (a concentrate from seedy varieties deteriorates more rapidly), and probably its maturity and environment during growth.

Since storage of frozen concentrated orange juice at 0° F. or below is recognized as highly desirable, it is advisable to provide additional stability as insurance against inadequate refrigeration for brief periods during distribution or while the product is in the hands of consumers. One aid is the avoidance of excessive pressures during extraction and finishing of the juice (*323*). Most processors apply heat to evaporator feed juice to inactivate at least a portion of the pectinesterase present. Temperatures of 145° to 160° for 5 to 30 seconds have been used commercially. This materially delays clarification and gelation under adverse storage conditions. Heat has been applied by steam injection (*45*), as well as by tubular and plate-type heat exchangers (fig. 16). Cutback juice is not heated. Considerable information on the effects of various heat treatments on pectinesterase and concentrate stability is available (*33, 219, 338, 367, 368*).

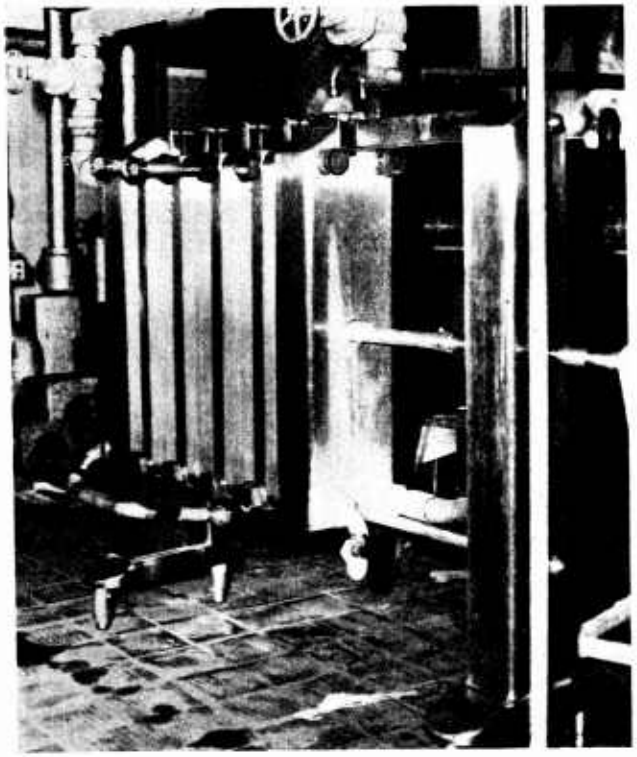


FIGURE 16.—Plate-type heat exchanger.

Opinions differ on the advisability of partial enzyme inactivation to provide increased stability. Some claim that this technique will increase the tendency of handlers to use lower quality fruit and to abuse the product. Some think that heating causes significant flavor damage, whereas others believe that any heat damage either is too small to be recognized by the average consumer (*354*) or is overshadowed by the better average condition of the product as purchased.

It has been observed (*33, 70, 219*) that increasing the concentration from the usual 42° Brix to 51° or 59° decreases the tendency of a concentrate to clarify. A high-density, frozen concentrated orange juice that is full flavored can be prepared by flavor fortification with cold-pressed peel oil (*355*). Developments in the field of low-temperature evaporation have also made possible the production of higher density products by the cutback process. Experimental studies have indicated that the higher density concentrates not only have more cloud stability but flavor stability tends to increase with concentration (*102, 355*).

Microbiology of Frozen Concentrated Orange Juice

Bacteriological control problems assumed real proportions when a rapidly expanding frozen-concentrate industry was started in 1945. The production of an ever-growing volume of unheated concentrate was accompanied by its quota of microbiological problems, which have reached the attention of both research and quality-control laboratories.

Although quality-control procedures vary from plant to plant, it is a common practice to determine the total microbial count of the finished product, and other determinations are included according to the dictates of the plant management. Bacteriological control methods used in one plant have been described (*27*), and the role of sanitation in the quality control of frozen citrus concentrates has been further discussed in a survey of methods used by 15 processing plants in Florida (*43*).

Total Counts.—Investigations of methods for the detection of total numbers of micro-organisms in citrus products have followed several different lines, including the development of suitable plating media, adaptation of the Frost little-plate method, a polaroscopic method, and the adaptation and development of direct microscopic methods.

The need for a standard plating medium for the examination of citrus products was predicated by the fact that different media were used by bacteriologists to obtain total counts (*181, 304*). Different incubation temperatures were used, which varied from room temperature to 86.0°-89.6° and even 98.6° F. This diversity of media and incubation temperatures was unfortunate, as it precluded uniform results from one laboratory to another. In selecting a medium for the enumeration of micro-organisms in citrus products, due consideration must be given to the fact that a diversity of microbial types may be found in the products and that many of them have rather fastidious nutrient requirements. It was concluded that no single medium would equally support the growth of all types of micro-organisms found in citrus products. The possibility exists that abnormally high counts resulting from a build-up of contamination in plant equipment might not be reflected in the counts obtained during routine examinations if a single medium were used (*181*).

The development of orange serum agar resulted in a medium that not only gives consistently high counts but favors the growth of certain organisms capable of multiplying in orange juice and causing undesirable changes (*28, 162*). A comparison of 18 different media has demonstrated that orange serum agar gives some degree of differentiation among yeasts, *Leuconostoc*, and lactobacilli organisms, and maximum counts are obtained (*304*). Orange serum agar is now available in a stable, dehydrated form (*412*).

Plate counts have the disadvantage that an incubation period of at least 2 days is required before many of the colonies develop to detectable size. Microbial buildups may occur in plant equipment during this incubation period, and the product may be damaged before the abnormal conditions are detected. This situation has given impetus to a number of investigations aimed at shortening the time necessary to detect abnormal microbial populations in the juice. One of these investigations was concerned with the possibility of using the oxygen uptake of orange juice as a means of estimating its microbial population (*172*). Although early results showed promise, subsequent experience with the method found little correlation between plate counts and oxygen uptake. It was believed that lack of correlation was due to differences in oxygen requirements by the different types of micro-organisms found in orange juice, and to the fact that these micro-organisms are not always present in the same proportions.

An adaption of the Frost little-plate method for the enumeration of micro-organisms in orange juice has reduced to 6 or 7 hours the time required to obtain a viable count. In this method inoculated orange serum agar is applied in a measured volume of the material to a definite area of a microscope slide. After incubation takes place, the slide is heated to dry the agar. It is then stained and examined under the microscope. Good correlation has been found between this method and regular plate counts (*369*).

Many investigations have been made to develop a satisfactory method for the direct microscopic examination of orange juice. One problem is that the juice may be washed from the slide during the staining process. The combination of a bacteria-free gelatin solution mixed with the juice helped to cement the film to the slide and made possible a more dependable enumeration of micro-organisms in the juice (*414*).

In the direct microscopic examination of frozen concentrated orange juice, a modification of North's aniline oil-methylene blue stain has been used by a number of bacteriologists (*162*). Two later methods recommend the mixing of a dilute stain solution with the juice and drying 0.01 ml. of the mixture on a microscope slide (*182, 480*). Slides prepared in this manner require no rinsing, and there is no danger of washing off the microbial cells. The principal difference between the last two methods is that one (*182*) uses 0.075-percent crystal violet stain solution and the other (*480*) uses a mixture of 10 ml. of North's aniline oil-methylene blue stain and 2 ml. of a 1-percent alcoholic solution of basic fuchsin, mixed and diluted to 100 ml. The latter method produces a preparation with greater color contrast and is preferred by many workers.

The phase-contrast microscope has been used for the direct microscopic examination of orange juice, but its use has been largely discontinued. The alinement of the phase microscope with its light source is very critical, and often considerable time is required to adjust the instrument properly. Also, particles of orange tissue of similar size and shape may be difficult to distinguish from microbial cells. At least one plant in Florida has a phase-contrast microscope and light source clamped into permanent alinement, which has been satisfactory for estimating the microbial quality of orange juice. However, most workers prefer to examine a well-stained slide under the conventional bright-field microscope.

All these methods have been used to obtain estimates of the microbial content of citrus products or to gain information regarding the bacteriological quality of the products. Fruit quality is of prime importance in the production of juice having good bacteriological quality. Orange juice aseptically produced from "soft rot" fruit had an initial viable count of 2,500 times that of juice prepared from apparently sound oranges (*483*). The necessity of thorough sorting and eliminating unsound fruit has been indicated by reports of high plate counts from juice aseptically extracted from oranges that appear normal on casual examination but upon more careful observation were found to have soft spots (*162*). Other work has shown that certain acid-tolerant bacteria will multiply when inoculated into oranges on the tree, and that juice with high microbial content may be obtained from these oranges even though they appear to be sound, normal fruit (*113*).

Although the fruit itself may be largely responsible for the wide variation in microbial numbers often found during the course of a day's operation, the role of adequate sanitizing of plant equipment in the production of concentrates of good microbial quality cannot be neglected (*27, 162*) (also see p. 43).

Off-Odor and Off-Flavor Spoilage.—A microbial spoilage characterized by a "buttermilk" odor and flavor has proven troublesome at times in the manufacture of frozen concentrated orange juice. It is caused by the growth of certain lactic acid bacteria in the juice. The lactic acid and diacetyl produced by these organisms are responsible for the buttermilk flavor. A method for detecting this type of spoilage is based on a colorimetric estimation of diacetyl (*182, 469*). The bacteria involved

have been identified as *Lactobacillus brevis, L. plantarum* var. *mobilis, Leuconostoc dextranicum*, and *L. mesenteroides* (*162*). Rapid means for generic identification of the organisms causing buttermilk flavor in frozen concentrated orange juice have been investigated (*29*).

Control measures consist of thorough washing and sorting of the fruit, thorough cleaning of fruit- and juice-handling equipment, and frequent sanitizing of the evaporators. Much of the trouble from these bacteria comes from their growth in adhering material in the evaporators, and when careful attention to plant sanitation and fruit sorting does not eliminate the source of the trouble, it may be necessary to flash-heat the evaporator feed juice.

Bacteria of Sanitary or Public-Health Significance.—Man's concern with his physical well-being has led to investigations of the survival of pathogenic bacteria in orange juice. Survival of enteric pathogens in orange juice was found to be dependent on the temperature at which the juice is stored. At low temperatures (25° F.) certain of the enteric pathogens survived for several days in single-strength juice, whereas at normal temperatures the hydrogen ion concentration (pH) of the juice proved to be rapidly lethal to the micro-organisms (*22*). When concentrated orange juice was inoculated with pathogens and with fecal material and then frozen for 48 hours, *Escherichia coli, Salmonella typhosa*, and *Shigella paradysenteriae* could not be isolated (*138*). Enterococci were found to survive in frozen orange concentrate longer than the other enteric organisms. However, the micrococci found in uninoculated concentrate were not predominantly of the type common to the intestinal tract (*211*).

Because coliform organisms are used by public-health workers as an index of human contamination, a number of investigations have been made of the incidence, significance, and survival of coliforms in frozen citrus juices (*27, 28, 112, 138, 139, 264, 274, 320, 327-329, 430, 479, 481-483*). Several papers have appeared on methods of isolating these organisms, especially *E. coli*, from frozen concentrates (*28, 274, 481, 483*). The most satisfactory method uses boric acid broth as the initial enrichment medium (*449*).

All types of coliform organisms have been found in frozen single-strength and concentrated orange juices, but the *Aerobacter* types were more common than was *E. coli* (*320, 328, 481, 483*). They are also associated with unsound or damaged fruit (*329, 483*). In one study on the sources of coliform organisms in citrus products it was established that the bacteria may be associated with scale infestations, fruit with slightly decomposed areas, ruptured fruit, and fruit flies (*328*).

Coliform organisms have been found to survive in frozen concentrated orange juice for extended periods when the storage temperatures are maintained at 0° F. or lower. When subjected to fluctuating temperatures encountered in the distribution and marketing of the product, the coliforms die off more rapidly and should be largely eliminated by the time the juice is consumed (*27*). Also, the flash-heating of the evaporator feed juice, which is now widely practiced, acts as a further safeguard against coliform contamination of frozen concentrate.

FROZEN CONCENTRATED LEMON JUICE

This is a pure-juice product made by concentrating single-strength juice in a low-temperature evaporator (p. 40), chilling to around 30° F. by passage through a heat exchanger, filling into drums lined with polyethylene bags, and freezing at —10°. Sometimes the chilled concentrate is filled into cans and frozen for institutional uses.

FROZEN CONCENTRATE FOR LEMONADE

Frozen concentrate for lemonade is rapidly becoming a leading food item. Unlike orange juice, lemon juice is always diluted with water and sweetened before drinking as a beverage. Frozen concentrate for lemonade has the proper amount of added sugar to reconstitute this product as a ready-to-drink lemonade. The frozen concentrate is principally a single-strength lemon juice with sugar added. However, since most people prefer a tartness in lemonade, the acid content of the product is adjusted by the addition of a small amount (approximately 10 percent) of concentrated lemon juice to give the proper balance of sugar and citric acid.

A typical frozen concentrate for lemonade would be prepared as follows: Add sufficient concentrated lemon juice to 280 gallons of single-strength lemon juice and 2,800 pounds of granulated sugar so that each 100 gm. of the final product will contain from 3 to 3.5 gm. of citric acid. This will make approximately 500 gallons of 55°-Brix concentrate. The concentrate is reconstituted to lemonade by adding 4 volumes of water to each volume of concentrate.

It is desirable that some juice cells should be added to this concentrate to improve the appearance of the reconstituted lemonade. This is done by screening juice cells from juice after

extraction and mixing them into the concentrate.

FROZEN CONCENTRATE FOR LIMEADE

Frozen concentrate for limeade was introduced to the trade in 1951. It consists of lime juice to which sucrose has been added to raise the Brix to about 48°. Some processors apply a mild heat treatment during preparation, and subsequently freeze and store the product at 0° F. or lower. On reconstitution with 4 to 4½ parts of water, an excellent limeade is obtained. As limes vary somewhat in solids and acid characteristics, some processors concentrate batches of juice for blending to maintain a uniform acid content in the finished product. Then by the addition of sugar to a 48°-Brix level, a uniform composition is attained. When properly prepared the product is excellent and has been well received by the public. Two additional lime-juice products were developed by the United States Department of Agriculture in 1954 (*35*), at least one of which is now in commercial production.

During concentration of lime juice much of its characteristic aroma and flavor are lost. Efforts to regain the original flavor through the addition of fresh juice, as is the practice in the production of frozen concentrated orange juice, or through the use of emulsified lime oil were unsatisfactory. The use of lime puree (p. 49) in amounts sufficient to give an oil content of 0.003 percent in the reconstituted limeade proved most satisfactory. The two products prepared by this method (*35*) include an 8-fold sweetened concentrate, which requires only the addition of 7 parts of water to prepare the beverage, and a more concentrated product, which is diluted to 35 times its volume by the addition of sugar and water. Preparation of the products is as follows:

To make 100 gallons of an 8-fold sweetened superconcentrate, use 6 gallons of lime puree, 42 gallons of a 2.06-fold concentrated lime juice, and 691 pounds of beet or cane sugar. For the finished beverage add 7 volumes of water to 1 volume of the sweetened superconcentrate.

To make 100 gallons of an unsweetened superconcentrate, use 26.3 gallons of lime puree and 73.7 gallons of a 5.12-fold concentrated lime juice. For the finished product add 30¼ pounds of sugar to 1 gallon of the superconcentrate and dilute to 35 gallons.

FROZEN CONCENTRATED TANGERINE JUICE

Tangerines are handled in the same manner as described under canning of tangerine juice (p. 29). Adjustment of extraction machines is necessary to accommodate tangerines, and the yield of juice is only about half that from oranges. To keep evaporators running at full capacity it is therefore necessary to have about double the number of extractors used for oranges. Frozen concentrated tangerine juice shows little tendency to gel, and it is unnecessary to heat-inactivate enzymes prior to concentrating.

FROZEN CONCENTRATED GRAPEFRUIT JUICE

Production is carried out with essentially the same equipment as for frozen concentrated orange juice. Frozen concentrated grapefruit juice has a tendency to gel or clarify because of the presence of pectinesterase (p. 6), and therefore the juice is heated to 150°-180° F. for a few seconds before it goes to the evaporator. Both sweetened and unsweetened frozen concentrates are produced commercially.

Frozen Purees

Frozen fruit purees for use in frozen desserts, baked goods, and other foods have been in commercial production since 1937. Citrus fruits, however, have not been included among such products, largely because they were thought to be too strongly flavored, would not keep well in storage, and would develop a "terpeny" off-flavor because of the high oil content resulting from the use of whole fruit in the pureeing process. However, it has been shown that frozen citrus purees, if properly prepared, will not develop off-flavors (*23, 31*), and such products are now being produced commercially in California and Florida.

Freezing preservation of citrus-fruit purees has proved to be a highly efficient and economical method for the preparation of fruit bases possessing natural flavors, color, and nutritive value. These sweetened or unsweetened fruit bases can be kept in good condition at 0° F. for more than a year, with very little, if any, loss of the original vitamin C content. The frozen puree can be defrosted, some of it used, and the rest refrozen without injury to color and flavor, provided it is not exposed to the air for long periods and is not allowed to remain at room temperature too long.

The processing method developed for the preparation of frozen citrus purees is a comparatively simple but effective means of retaining color and flavor in the finished product. Sound, fully mature fruit is first thoroughly washed, preferably with a good detergent, and rinsed well with clean cold water to reduce microbial contamination to a minimum. With certain citrus varieties purees made from immature fruit have a tendency to be bitter.

Medium to small fruit is preferred because of the better yield and quality of the juice. After the fruit is washed, the stem end may be cut off and discolored spots removed so that no dark specks will be mixed in with the bright-colored puree. If Washington Navel oranges are used, the navel end should first be removed.

After the whole fruit has been trimmed, it is either crushed in a machine, such as an apricot pitter, or sliced by means of circular saws. The crushed or sliced fruit is then put through a rotary (*247*) or tapered screw press fitted with stainless-steel screens of appropriate mesh, so that most of the fruit is reduced to the form of a puree. Other machines may be available to accomplish the same purpose. Screen openings of 0.027 to 0.044 inch in diameter are usually employed, depending on the end use of the puree. Screen sizes of 0.027 and 0.033 inch are preferable when purees are intended for sherbets, ices, pies, and beverages, but larger sizes are better for purees intended for marmalades, jams, cake, and sundae toppings.

Yield of puree from the whole fruit is approximately 50 to 60 percent, and should contain 0.40 to 0.75 percent of peel oil depending on the variety of fruit. With some lots of fruit the peel-oil content of the puree may be considerably higher and too strong for most uses. Then the oil content of the puree can be controlled if various proportions of the fresh fruit are passed through an abrasive machine prior to crushing to remove most of the oil sacs or flavedo. Another method of standardizing the oil content of purees is by adding different proportions of single-strength juice.

After a puree of the required oil content is obtained, it is run into a stainless-steel tank, and dry sugar gradually added with thorough mixing in the proportion of 1 part of sugar to 5 parts of puree. Purees may be packed without the addition of sugar. The sweetened or unsweetened puree is filled into enameled tin containers of 1 to 2½ gallons' capacity, the cans are hermetically sealed or closed with slip tops, and the contents are frozen at subzero temperatures. The product is stored at 0° to —10° F. The time of freezing can be reduced if the puree is first frozen to a slush in a mechanically agitated heat exchanger before filling into cans.

Orange, tangerine, lemon, and lime purees have been successfully used in the commercial preparation of milk sherbets and water ices. However, taste tests have indicated that milk sherbets that contain approximately 2.5 percent of butterfat have a more pleasing flavor and texture than water ices. In sherbets and ices made from citrus purees, minute pieces of orange, lemon, and lime peel are detectable, which provide visual evidence to the consumer that the products are flavored with natural fruits.

Lemon puree is particularly useful as a flavor base for lemon pies. Frozen purees also have been used in the preparation of puddings and cakes. Lemon and lime purees have been used by the beverage trade for the manufacture of ades and similar fruit drinks.

Powdered Citrus Juices

The dehydration, or drying, of citrus juices to a powdered form has been of considerable interest for many years because of the numerous advantages of such a product. It has been accomplished by several methods, but it appears that in addition to the quality of the powder the economics of the drying process will dictate the commercial success of any process or combination of processes. Since citrus juices consist largely of water, it is not economical to attempt to dry them directly to a powder. A more economical procedure is first to concentrate the juice in a vacuum evaporator, then remove the remaining water by a vacuum drying process to avoid heat damage to the flavor. The sixfold concentrate now being produced by low-temperature evaporation for the manufacture of frozen citrus concentrates provides an excellent starting material for the preparation of a powder (*263*).

Citrus-juice concentrates have been converted to powdered form by spray-, drum-, and freeze-drying. However, dehydration was accomplished by the addition of drying aids to promote the rate of drying, to counteract hygroscopicity of the dried product, and to reduce the tendency of the powder to cake during storage. Although drying aids, such as carboxymethylcellulose (*105*) and glyceryl monostearate (*416*), in concentrations as low as 1 percent on a total-solids basis have been used experimentally, the results were characterized by low yields, flavor changes, and a powder difficult to reconstitute. Other drying aids, such as corn-sirup solids, pectin, and whey, have been used, but in such large amounts that they altered the nature of the powder.

During World War II lemon juice mixed with corn-sirup solids was spray dried commercially, and a powder was produced that contained about 20 percent of lemon-juice solids and 80 percent of corn-sirup solids. In addition, some lemon oil and crystalline ascorbic acid were added to the dry powder before packaging. This product is still being produced as a flavor base for the confectionery and soft-drink trades. Later an orangeade

powder was prepared by spray-drying, which contained 25 percent of orange-juice solids and 75 percent of corn-sirup solids (*188*).

Drum-drying has been judged unsuitable for preparing acceptable citrus-juice powders, since such powders are too difficult to reconstitute (*295*). High production costs and large capital investments in equipment have deterred the commercial exploitation of freeze-drying citrus juices to a powder (*56, 120*). Although powders prepared experimentally by freeze-drying were readily reconstituted, they were reported to show a tendency to cake and develop off-flavors during storage (*119*).

In 1943 a method was developed for the preparation of powders made from fruit juices mixed with corn sirup (*175*). This method was the forerunner for the development of several processes in which citrus juices were dried in a puffed, or expanded, form (*51, 159*). One of these methods consisted of spraying 50°-Brix orange concentrate on the walls of a jacketed, cylindrical, vertical drier under a vacuum (*71, 379, 382*). The film of concentrate on the walls was of a thickness representing a yield of 0.26 pound of dried powder per square foot. Water at approximately 125° F. was circulated through the jacket during drying. The concentrate was allowed to dry until it reached the desired moisture content, then it was scraped off the walls and removed through an air lock into an airtight dolly. For a given cycle time a single drier could be duplicated to give a sufficient number of units so that the concentrate could be charged to the system and the powder removed continuously.

A commercial plant was constructed with a capacity of 5,000 pounds of powder per 24 hours, in which the normal operation was to charge each drier in succession, dry under an absolute pressure of 400 to 600 microns for 2 to 6 hours until it reached the desired moisture content, discharge the driers, and repeat the cycle. The powder was usually removed at 1.5- to 2.5-percent moisture levels. In-package desiccation was used to increase stability (*71*), a technique previously described by Howard (*190*).

In 1947 a continuous belt-type vacuum drier was specially designed for drying orange juice in a puffed form (*399*).

A process employing a vacuum shelf drier has been described for the preparation of a dehydrated orangeade powder (*340, 416*). The juice was first concentrated in a vacuum evaporator to remove 97 percent of the water, then mixed with 2 to 2½ times its weight of dry sugar to form a moist granular mass. The addition of calcium carbonate in a ratio of 1 part to 8 parts of acid in the juice aided drying. Sufficient ascorbic acid was added to the mixture to provide a total of 0.05 percent in the finished beverage. This mixture was dried in shallow pans in a vacuum shelf drier at 122° F. at about 20 mm. of pressure. Its moisture content was reduced to 0.5 percent. Sufficient anhydrous citric acid was added to give a citric acid content of 3.5 to 4.0 percent.

The addition of 0.006 percent of fivefold concentrated orange oil in the form of a 10-percent extract gave an acceptable flavor with good stability. The dried powder was reconstituted by adding 6 or 7 parts of water to 1 part of powder. Samples showed an almost complete absence of darkening during storage for 5 months at 98.6° F.

Later a method was developed by the United States Department of Agriculture for puff-drying liquid materials in a vacuum shelf drier at approximately 1 mm. of mercury pressure in such a manner that the product puffs during drying to form an expanded honeycombed or spongy structure (*417, 418*) (fig. 17). The feed juice consists of 58°- to 60°-Brix orange concentrate produced by low-temperature evaporation. The concentrate is spread evenly over the surface of shallow trays to obtain a film approximately $\frac{1}{16}$ inch deep, or a tray loading of 0.5 pound per square foot. The shelf drier is so constructed that steam or hot water can be circulated through the shelves to supply heat to the trays of the concentrate. Temperatures encountered in a typical drying cycle in which the shelves were preheated to 200° F. and maintained at that temperature during the early stages are shown in figure 18.

After the product is dried for 90 to 100 minutes, the moisture content is reduced to about 3 percent, and then the product is cooled to below 90° F., the vacuum is released, and the trays are removed from the drier. During the drying process the original $\frac{1}{16}$-inch layer of concentrate has been expanded 15 to 20 times in volume. After the product is cooled, it is quite friable and is easily removed from the trays. It is very hygroscopic, and handling and packaging must be carried out in a room maintained at not more than 15-percent relative humidity to prevent uptake of moisture.

As previously pointed out practically all the characteristic flavor and aroma of citrus juices, particularly orange, are derived from volatile oils, most of which come from the peel (flavedo) of the fruit during extraction of the juice. These volatile oils are largely lost during concentration of the juice in the preparation of a powder, which is one of the principal reasons why most citrus powders prepared to date have been lacking in natural flavor and aroma. The success of the United States Department of

FIGURE 17.—Orange juice is dried in a vacuum shelf drier under a high vacuum so that the product puffs to form an expanded spongy structure.

Agriculture method for preparing orange powder is largely dependent on the manner of returning to the powder essential flavoring oils lost during processing.

A process for incorporating fruit flavors and flavoring oils into sorbitol has been patented (*134*). In this process orange oil is added slowly to molten sorbitol, which has been heated to about 392° F. to remove water and then supercooled to around 194°. The emulsion of oil in liquid sorbitol is then allowed to crystallize, and the mass crushed to granules 10 to 20 mesh in size. The sorbitol-oil granules are then mixed with the orange powder before packaging. Further research by the United States Department of Agriculture has shown that glucose or sucrose could be used in place of sorbitol.

In-package desiccation appears to be indispensable to the preparation of a stable orange-juice powder. It is accomplished by sealing orange powder of 3- to 4-percent moisture as it comes from the drier in a hermetic container with a sufficient amount of desiccant to reduce the residual moisture in the powder to 1 percent or lower. The desiccant, calcium oxide or calcined lime, is enclosed in a siftproof, moisture-permeable paper container, which permits transfer of water vapor from the product to the desiccant without contaminating the product. This desiccant will react with 32 percent of its weight of water during conversion to calcium hydroxide and will maintain virtually zero humidity until completely reacted. Since calcined lime will increase in volume on rehydration, the container must be so constructed that it will not burst with the expanding lime and contaminate the product (*166*).

Experiments have indicated that puffed orange powders could be produced with a continuous belt-type vacuum drier, and a commercial plant was built that utilized this type of equipment. Orange powders, with and without the addition of drying aids, were produced with both shelf and belt-type vacuum driers under conditions that caused the concentrate to puff during drying (*4*).

Samples of orange powder prepared by puff-drying and containing 40 percent of added corn-sirup solids were stored at 70°, 90°, and 100° F., and assayed periodically for chemical

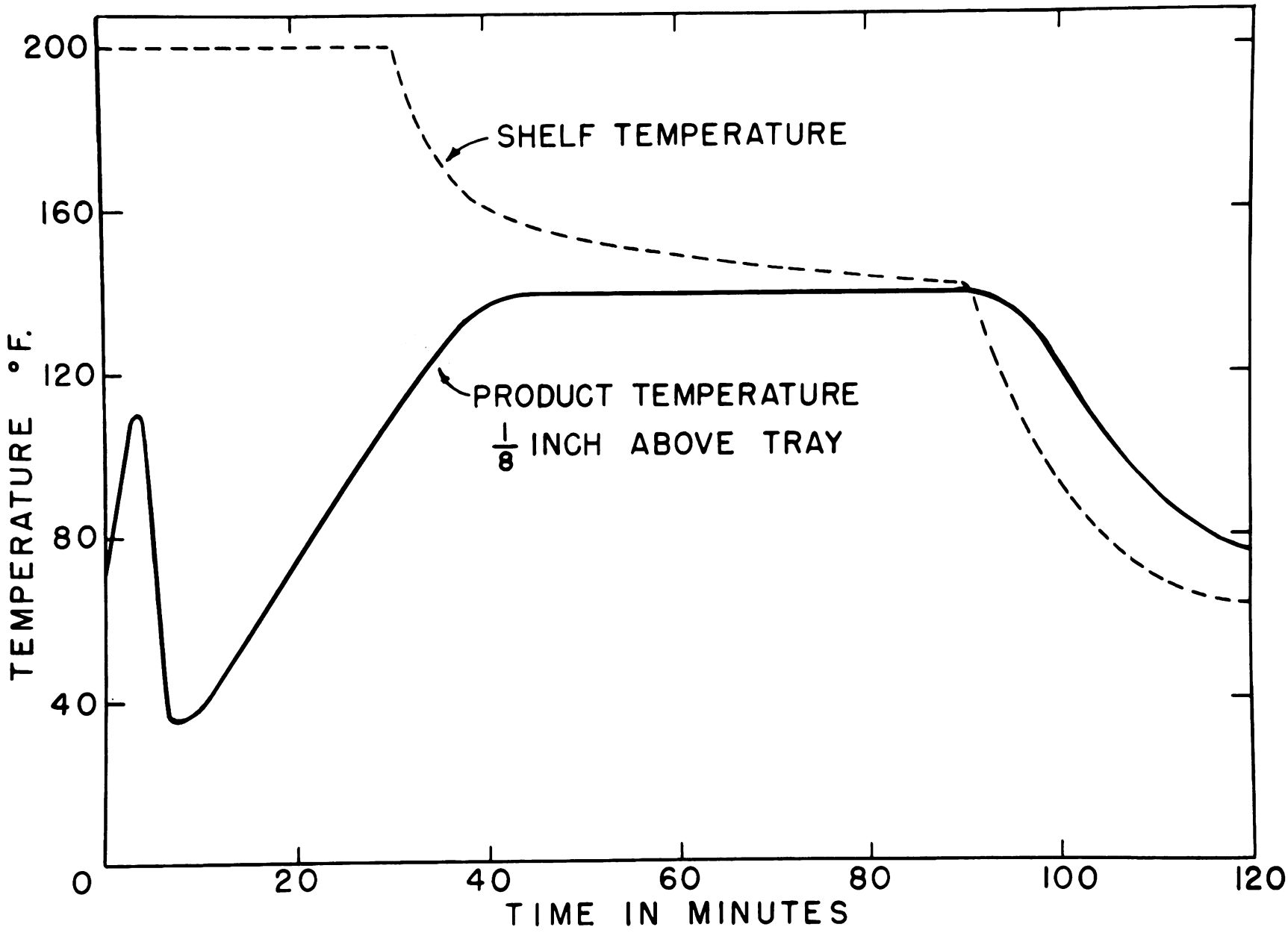


FIGURE 18.—Time-temperature cycle for converting 60°-Brix orange concentrate into orange powder of 3-percent moisture content, with a tray loading of 0.5 pound per square foot and at 2 mm. of pressure.

and organoleptic changes (*306*). In-package desiccation that reduced the moisture content of the powder to 1 percent or lower was very effective in reducing flavor deterioration, undesirable color changes, and loss of ascorbic acid during storage. Incorporation of the orange oil in sorbitol was effective in stabilizing the added oil during storage. Samples of orange powder were still acceptable after 6 months' storage at 100° and had changed very little after 1 year at 70°.

CITRUS BYPRODUCTS

Pectin

PECTIN MANUFACTURE

Over 2 million tons of citrus peel, containing about 3 percent of pectin on a fresh-weight basis, is produced each year in the United States as a byproduct of the citrus-processing industry. Approximately 5 million pounds of citrus pectin is produced yearly from this source, mainly in California.

Pectin manufacture is an expensive and complicated process, consisting of numerous batch-type operations, use of corrosive chemicals and expensive solvents, and filtration of exceedingly viscous solutions. The principal steps include preparation of the peel for extraction or storage for later use; removal of bitter glycosides and crude sugars; conversion of protopectin in the peel to soluble pectin; filtration of extracted pectin; and precipitation, purification, and drying of the prepared pectin.

Citrus peel employed for pectin production is usually that from which peel oil has previously been removed. Peel is first comminuted or minced to facilitate washing and extraction. If the peel is not extracted immediately, it is heated to 104°-108° F. for about 10 minutes to inactivate pectic enzymes, and then dried for storage. Otherwise, inactivation of pectic enzymes is accomplished during the extraction step. The minced or dry, stored peel is washed copiously with water until all glycosides and sugars are removed. Some water-soluble pectin already in the peel may be extracted during washing, but it is of little consequence as this pectin is usually of a low jelly grade.

Pectin extraction is performed by placing the prepared peel in vats of water, where the slurry is brought to a boil, and concentrated hydrochloric or sulfuric acid, previously diluted to prevent local overheating, is added to adjust to about pH 2.0. Because of the strong binding power of pectin for polyvalent metal ions, extreme care must be exercised in later purifications when sulfuric acid has been employed in order to remove the traces of lead, which are always found in this technical reagent.

The acid slurry is heated at 200° to 212° F. for 45 to 60 minutes. During this time protopectin is converted by "restricted hydrolysis" to pectin, which is extracted into the solution. Too high an acidity or too long an extraction at these temperatures may result in an undesirable degradation of the pectin. In general, several extractions of a given lot of peel under mild conditions are preferred to a single extraction under severe conditions of time, temperature, and acidity.

The extract obtained may contain approximately 1 percent of pectin. If the concentration of pectin in the extract is low, it may be evaporated under low-temperature conditions to a pectin content of 3 to 4 percent to facilitate subsequent precipitation.

Filtration of the extract is a tedious process, because the extract is corrosive and the pectin solutions are viscous. Some type of filter aid must be employed, which usually consists of shredded paper or diatomaceous earth added during the extraction treatment or before filtering. Filtration is carried out in two stages. An initial coarse filtration removes the large pieces of pulp and other coarse material, after which a fine filtration produces a clear filtrate. Continuous drum and plate-and-frame filters (fig. 19), in conjunction with vacuum and pressure, are ordinarily used in the filtration procedures. The corrosive nature of the acid extracts necessitates the use of inert structural materials, such as stainless steel for the equipment and Orlon and Dynel fabrics for the filter cloths.

The extracted pectin is next purified by precipitation from solution and careful washing. It is sprayed or blended into tanks containing any one of several organic solvents, such as ethanol, acetone, isobutanol, or isopropanol, where the pectin precipitates as a gelatinous mass. The amount of solvent employed is such that there will be a final concentration of 50- to 70-percent solvent in the tank after the pectin extract is added.

The precipitated pectin is freed from the solvent by pressing (fig. 20) and/or by the action of drain screws or roll presses used to convey the pectin precipitate to a series of washing vats. After several washings in 50- to 70-percent solvent-water mixtures, the pectin is given a final dehydrating wash in 80- to 90-percent solvent. The washed pectin is drained and pressed to remove up to 50 percent of the solvent and water present, and it is then dried in warm air or on a heated drum to a moisture content of 6 to 10 percent. The dried pectin

FIGURE 19.—Filtering pectin extract in plate-and-frame filters. (Courtesy of Sunkist Growers, Inc., Los Angeles, Calif.)

is ground to pass a 60-mesh screen, and packaged for marketing (fig. 21). Some citrus pectin is sold as a liquid product in solution with added citric acid.

In an efficiently operated plant the apparent high cost of solvent is considerably reduced by employing solvent recovery and repurification throughout all stages of precipitation, washing, and drying. An excellent and detailed description of this process for pectin manufacture has been given by Hull et al. (*192*). Additional information has been reported by McCready and Owens (*259*).

Salting-out with high concentrations of polyvalent metal salts is an alternate method sometimes employed for precipitating pectin from its extracts. In this process a mixture of aluminum hydroxide and chloride and ammonium sulfate is added to the pectin extract, causing the pectin to precipitate as a gel. When this process is employed, there is a greater need for careful washing with acidulated alcohol to remove the strongly bound aluminum ion and the ammonium sulfate. This method of pectin manufacture has been fully described elsewhere (*209*).

Because of natural variations in the peel of different citrus fruits, the process of pectin manufacture is made flexible, so that by employing different conditions of extraction and by blending various batches a uniform grade of product may be obtained. Pectins normally obtained by the described process are the so-called rapid-set pectins, which gel very quickly. This type of pectin is desirable in the manufacture of jams and preserves containing pieces of whole fruit that might collect at the top of the jam or preserve if it gels slowly. However, for other types of jams and jellies manufacturers prefer a pectin that will not gel until the bottled products are in storage and will not have to withstand the shock of too much handling. The so-called slow-set pectins are made by a slight variation of the normal manufacturing process for pectin. The pectin extract obtained in the standard manner is allowed to stand 10 to 20 hours at 30° to 40° F. in a strong acid bath before precipitation and purification. This treatment is believed to result in a slight demethylation of the pectin and perhaps some reduction in molecular weight, which gives the pectin the slow-setting properties desired.

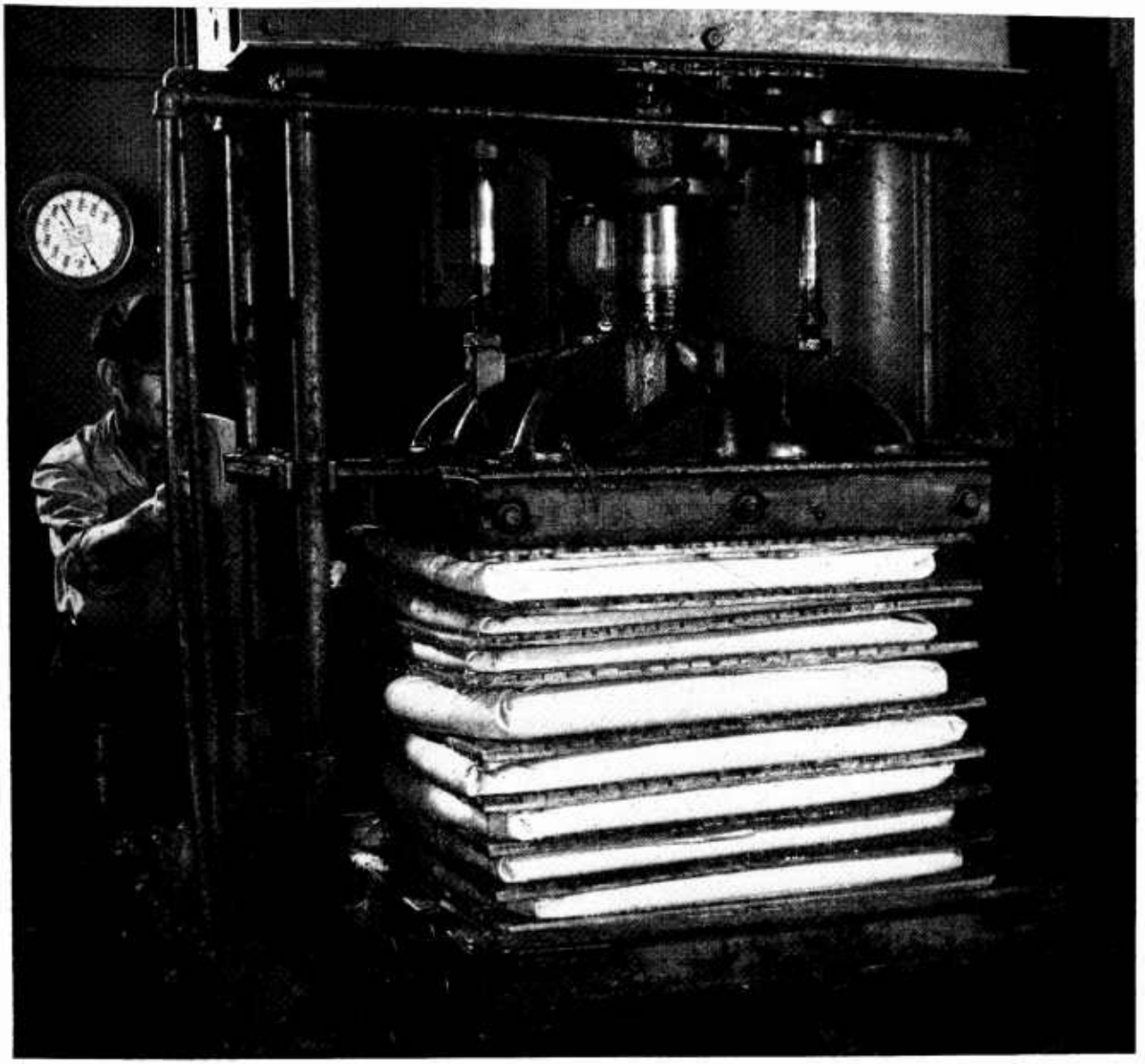


FIGURE 20.—Pressing solvent from precipitated pectin. (Courtesy of Sunkist Growers, Inc., Los Angeles, Calif.)

The value of commercial pectins is determined principally by their ability to form jellies. Pectins are therefore standardized before marketing with respect to their jelly-forming ability. This standard is called jelly grade, and is a number that represents the pounds of sugar that 1 pound of pectin will support in an approximately 65-percent sugar jelly containing small amounts of acid. Pectin grades are determined by preparing a series of 65-percent sugar jellies under carefully defined conditions and rigidly defined composition (*222*). Different proportions of the pectin are used in the series of jellies, which are later compared visually with a standard jelly. From the minimum amount of pectin employed in producing a jelly essentially like the standard jelly, the jelly grade is computed to pounds of sugar per pound of pectin. Thus the expression 200-grade pectin refers to the fact that 1 pound of 200-grade pectin will support 200 pounds of sugar in a 65-percent sugar-solids jelly of standard quality. One pound of a 100-grade pectin will support only 100 pounds of sugar. A liquid pectin of 50 grade means that 1 gallon will support 50 pounds of sugar in a 65-percent sugar-solids jelly of standard quality.

FIGURE 21.—Packaging dried citrus pectin. (Courtesy of Sunkist Growers, Inc., Los Angeles, Calif.)

USE OF PECTIC SUBSTANCES

The most important use of pectic substances is in the commercial and home production of jams and jellies. Approximately 6 million pounds of dry pectin is produced yearly for this purpose alone, of which over three-fourths is derived from citrus fruit. Apple pectin accounts for approximately one-fourth of the total production.

Pectins have many other uses in small amounts, which depend on their remarkable abilities to form and stabilize emulsions, in addition to the fact that they are a normal constituent of foods and may therefore be safely ingested. Pectins have been used as thickeners and stabilizers in milk products, as chocolate milk, and as emulsifiers in cosmetics, cold creams, and soaps (*222*). Pectin has also been suggested in some cases as a carrier for drugs that are injected intramuscularly. The function of pectin is to delay absorption of the drug to enable a more prolonged effect, such as in insulin-pectin preparations and pectin-penicillin preparations (*222*).

Pectin and its derivatives appear also to have certain inherent therapeutic properties, particularly in certain cases of malfunction of the digestive tract. Pectin preparations have been employed as a supportive measure in cases of infant diarrhea and other alimentary-tract disorders (*478*). During World War II it was found that dressings of 2-percent pectin solution were one of the most effective means of treating tropical sores of vague etiology, and very satisfactory results have also been reported (*160*) in the treatment of deep and superficial wounds, where pectin-solution treatments appeared to accelerate healing by promoting epithelization. Other medicinal applications of pectin or its derivatives, particularly in Germany, have included use as a hemostatic agent and as a blood-plasma substitute (*222*).

LOW-METHOXYL PECTINS

These pectins contain from 2.5 to 5.0 percent of methoxyl groups by weight. Low-methoxyl pectins and pectic acid may be obtained by modifying the regular process of pectin manufacture. The modifications consist principally of treating the pectin at some stage of manufacture with hot concentrated acid, cold alkali, or the enzyme pectinesterase. The pectin may be demethylated while it is still in the peel in the form of protopectin by extraction with alkali in place of acid or by directly treating the extract containing pectin with acid, alkali, or pectinesterase. Usually demethylation is accomplished by treating the pectin extract with hot acid or cold alkali. Demethylation at this stage has the advantage that the low-ester pectin or pectic acid, depending on the extent of demethylation, will spontaneously precipitate in the acid solution or can be precipitated from the alkali-treated solution by reacidifying and adding traces of calcium or other polyvalent cations. The low-ester pectin precipitate may then be washed with acidulated water or very dilute acidulated alcohol solutions instead of large amounts of alcohol as required in the purification of fully methylated pectins. A final washing with acidulated 70-percent alcohol is usually sufficient to remove the traces of cation employed to aid precipitation of the low-ester pectins.

Commercially employed processes of manufacturing low-ester pectins still involve many trade secrets, and careful control of times and temperatures as well as concentrations of acid or base must be exercised to obtain the desired degree of demethylation without otherwise degrading the anhydrogalacturonide chain. Pectic acid is, of course, produced by the same process simply by allowing demethylation to proceed to completion. Excellent descriptions of procedures for the manufacture of low-ester pectins are available (*133, 259*).

Low-methoxyl, or low-ester, pectins are becoming increasingly important owing to their ability to form low-solids jellies, such as tomato aspic, by the addition of traces of calcium or

other polyvalent cation. Besides their uses in low-solids jellies, low-ester pectins are useful in compounding cold puddings and in forming films for coating nuts, candies, and other food products. Pectic acid is sometimes used in the pharmaceutical industry for compounding quick-dissolving tablets or pills.

PECTATE PULP

Although not a pure pectin preparation, pectate pulp should be mentioned. This product is a form of leached citrus peel, containing principally low-ester pectins and pectic acids, crude cellulose, hemicelluloses, and other peel constituents of high molecular weight. Pectate pulp is prepared by treating citrus peel with soda ash, after which it is washed, dried, and ground. Pectate pulp may be dispersed in water by adding phosphate salts, and may be caused to flocculate under a wide variety of conditions, and thus it is made useful for recovering or removing suspended matter from solutions. In addition, pectate pulp may be used in adjusting the viscosity of quenching baths for tempering special steels, as an aid in creaming rubber latex, and in formulating oil-well drilling muds (*192*).

Citric Acid

Although all varieties of citrus fruits contain citric acid, only lemons are used in its manufacture in the United States. Citric acid is found free in the juice, but it cannot be separated directly. Attempts have been made to do this, but all have been unsuccessful (*66, 333*).

The manufacture of citric acid from lemon juice has been practically replaced in the United States by a mycological process (*214, 455*), beet molasses being utilized chiefly as the raw material. Of a total United States output of 50 to 60 million pounds annually, approximately 2,000,000 pounds of citric acid and 3,330,000 pounds of calcium citrate are still produced from lemons in California (*187*). The process is based on the precipitation of citric acid as a calcium salt and decomposition of the calcium citrate with sulfuric acid. The various steps in the production of citric acid are shown in figure 22.

Undergrade, or cull, lemons from the inspection tables of citrus-processing plants or surplus lemons during a season of overproduction comprise the raw material. This material is conveyed to lemon grinders (fig. 23), where the juice is separated from the chopped peel. The rag, seeds, and pulp are removed in perforated rotary reels. The rag, wet with juice, is extracted further in a finisher, and this juice is combined with the reel juice. The combined juices are then partially deoiled in centrifugal separators.

A specified amount of juice discharged from the centrifugals is pumped to a still, where oil is removed by steam distillation. The deoiled juice is cooled, combined with the juice that has not been treated by steam distillation, and pumped to storage tanks as the raw material for citric acid recovery. This liquor is held in storage tanks (fig. 24) for about a week, during which time enzymes present degrade the pectin and allow the pulp particles to separate and congeal.

The clarified portion of the aged juice is pumped from the storage tanks to neutralizing tanks for further treatment. The pulpy scum from the surface of the tanks is pumped to special filter tanks, where it is boiled to bring about a coagulation of the pulp particles, and then filtered, the filtered juice being combined with juice in the neutralizing tanks.

To this juice filtered "C" liquor (see below) is added to fortify the acidity, since acid recovery will be higher and handling more efficient when the juice is of 6-percent acid content. The mixture is next heated and agitated to promote coagulation of the remaining fine pulp. An aqueous lime slurry is then added to precipitate citric acid as calcium citrate. The liming is carefully controlled to avoid overneutralization, a residual acidity of 0.05 to 0.2 percent being desirable. The slurry is filtered, the filtrate discarded, and the filter cake washed with hot water.

The calcium citrate can be made into citric acid immediately, stored for later manufacture into citric acid, or packaged for shipment as citrate. If it is to be stored or packaged, it is dried in a two-stage rotary drier and packaged in bags or stored in steel silos.

Citrate to be made into citric acid is conveyed to a decomposing tank containing wash water from a previous filtration. The slurry of calcium citrate obtained is carefully treated with sulfuric acid. As the calcium citrate is decomposed, citric acid is liberated, and the calcium combines with the sulfuric acid to form insoluble calcium sulfate (gypsum).

Filter aid is added and the slurry is filtered to yield a clear citric acid liquor containing about 25 percent of citric acid; this concentration is reduced to approximately 15 percent after washing the filter cake. The filter cake of calcium sulfate is discarded.

The weak citric acid liquor is fed to a stain-

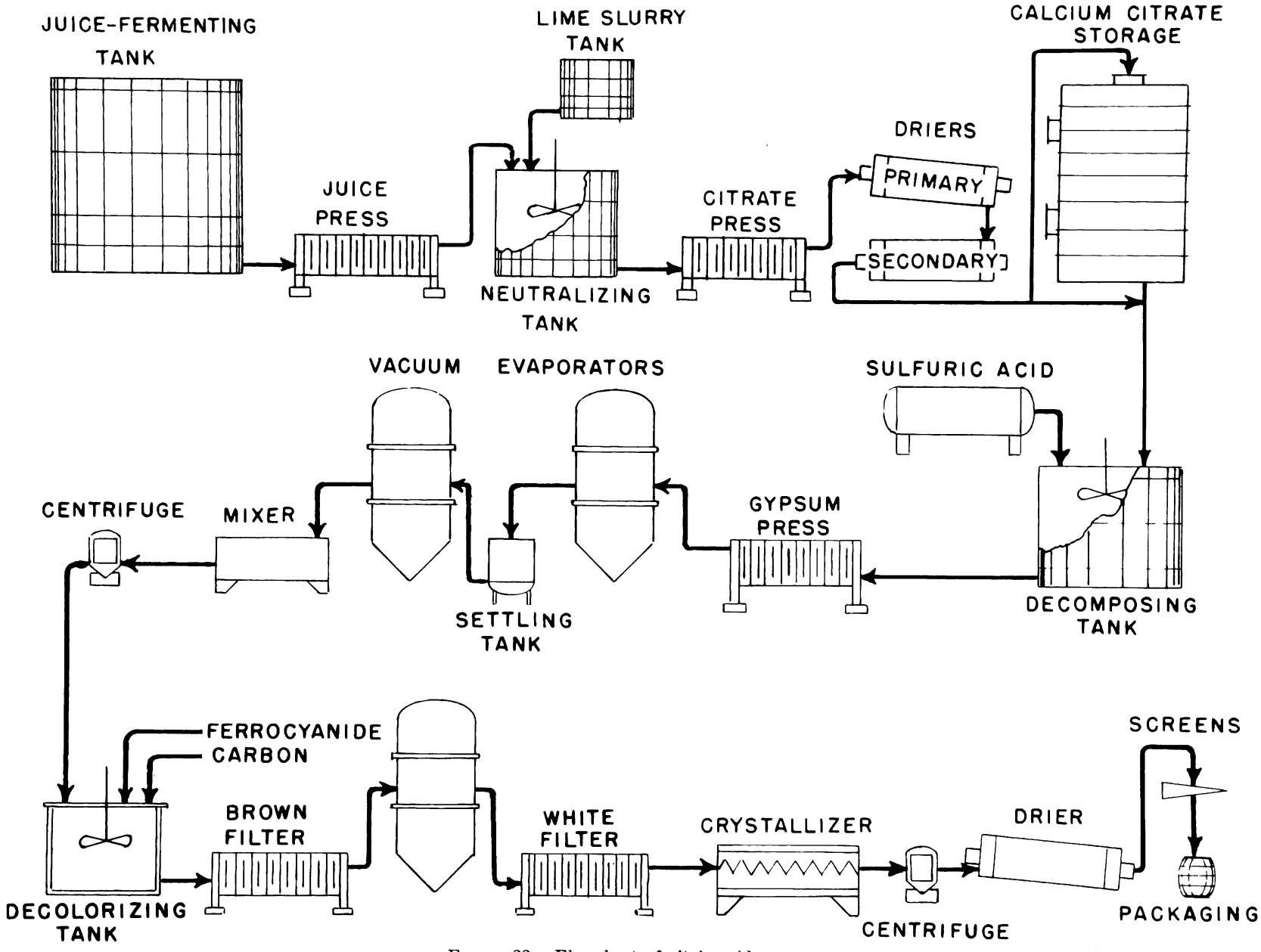


FIGURE 22.—Flowsheet of citric acid process.

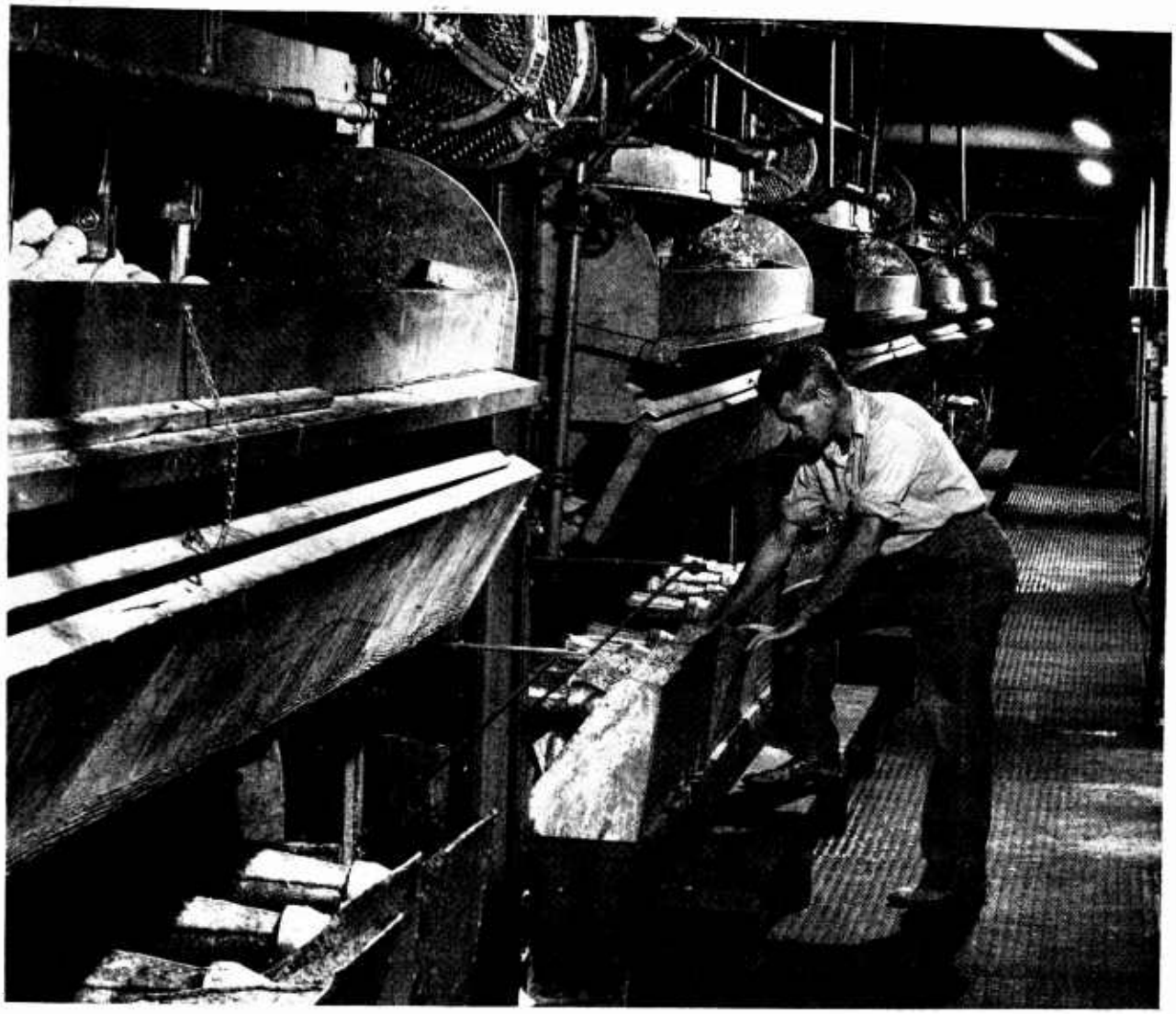


FIGURE 23.—Lemon grinders used in the preparation of citric acid. (Courtesy of Sunkist Growers, Inc., Los Angeles, Calif.)

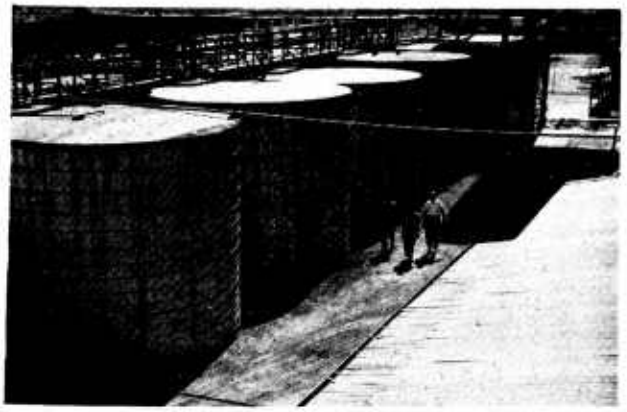


FIGURE 24.—Juice storage and fermenting tanks. (Courtesy of Sunkist Growers, Inc., Los Angeles, Calif.)

less-steel vacuum evaporator (fig. 25), where it is concentrated at 122° to 130° F. to about 30° Baumé. During concentration the calcium sulfate remaining in solution will precipitate. The concentrated acid liquor is pumped to lead-lined tanks, where the precipitated calcium sulfate is allowed to settle out. Clear concentrated liquor is drawn from this settling tank and fed to a stainless-steel, calandria-heated evaporator fitted with an impeller. Concentration of the acid is continued under vacuum at a temperature of 113° to 136° F. until a concentration is reached where, upon seeding with citric acid crystals, the concentrated acid is induced to crystallize as a crude brown grain of suitable size. This magma is discharged to a stainless-steel basket centrifugal and centri-

FIGURE 25.—Evaporators for concentrating citric acid liquor. (Courtesy of Sunkist Growers, Inc., Los Angeles, Calif.)

fuged partially dry. This crude acid is called "A" crystals.

The mother liquor from the "A" crystals is diluted to about 30° Baumé, and the vacuum-evaporation steps are repeated to obtain a concentrate from which "B" crystals are recovered. This second mother liquor is also diluted, settled, concentrated, and crystallized to obtain "C" crystals. The "C" liquor is too impure for further refining and is returned to the neutralizing step for recycling. The "C" crystals are dissolved in the weak liquor used for the first concentration, and recycled through the "A," "B," and "C" crystallization steps.

The "A" and "B" crystals are combined in a rubber-lined tank with white magma mother liquor and redissolved. After the mixture is adjusted to 30° Baumé, carbon is added for decolorizing and calcium ferrocyanide for removal of iron. The mixture is warmed and filtered to give a clear, colorless citric acid liquor, which is concentrated at 140° F. in a stainless-steel vacuum evaporator to 38° Baumé, mixed with filter aid, and filtered again so that the acid solution has a sparkling clarity.

The warm acid liquor is then pumped to open, horizontal, semicylindrical, jacketed crystallizers equipped with agitators. Cool water is circulated through the jacket at a slow rate to

FIGURE 26.—Centrifuging white citric acid crystals. (Courtesy of Sunkist Growers, Inc., Los Angeles, Calif.)

reduce the temperature of the acid solution. During this period a heavy batch of citric acid crystals grows in the liquor. This white magma is then centrifuged (fig. 26) and rinsed.

The centrifuged crystals are dried in a rotary drier with a stream of warm air. They are then screened into coarse granular, granular, or fine granular sizes, and packed into kegs and barrels for shipment.

Citric acid is the most commonly used organic acid in the food and pharmaceutical industries. Its salts, especially sodium salt, are widely used in medicines and foods as buffers and stabilizers. It is used extensively in effervescent salts, candy, soft drinks, metal pickling, water conditioning, and silvering of mirrors. The acid is also used as an ink ingredient in engraving, dyeing, and calico printing, and also in the preparation of paints and alkyd resins. The plastics industry uses large amounts of its esters as plasticizers.

Citrus-Seed Oils

It has been estimated that if all the seeds from citrus-processing plants in Florida alone were used for the extraction of oil, around 9 or 10 million pounds of oil would be obtained annually. However, only a small fraction of the seeds are so used, as most of them are dried with the waste cannery peel and rag to produce dried citrus-pulp stock feed (*197*) (see p. 73).

The seedy varieties of citrus fruit, such as seedling and Pineapple oranges and Duncan

grapefruit, contain about 3.5 percent of seeds, which in turn contain from 55 to 60 percent of moisture and about 15 percent of oil. The average proximate composition of air-dried citrus seeds, compiled from various published data, is as follows:

Constituent	*Percent*
Ash	2.48– 3.57
Crude fiber	5.41–17.79
Crude protein	6.94–15.94
Ether extract	21.88–34.44
Nonnitrogenous substances	22.21–44.63
Water	6.82–11.86

Citrus seeds are obtained from citrus-processing plants, where large quantities of fruit have been collected and utilized primarily for juice or sections. The seeds are obtained intimately mixed with rag and pulp but separate from the peel. Separation of seeds from the rag and pulp may be accomplished in several ways, but the difficulty of so doing is one of the chief deterrents to increased production of seed oil. Separation may be accomplished with a paddle-type finisher or similar equipment. Another procedure is to lime the mixture of seeds and wet pulp, as in the preparation of dried citrus feed, and dry in rotary driers. The seeds can then be separated from the dried pulp by screening and winnowing. The separated pulp is of value as feed.

Dried seeds from which the hulls may or may not be removed are passed through cracking rolls, and the oil is extracted in screw expellers of the type commonly used in preparing cottonseed oil and tung oil (*197, 318, 447*). These machines produce a press cake with an oil content ranging from 14 to 16 percent. The oil content of the press cake can be further reduced in these machines but at the expense of heat damage to the oil. More modern machines have been developed that will reduce the residual oil to 7 percent without heat damage, but these machines are not yet in general use. Solvent extraction would reduce the residual oil even further, but so far as is known this has not been attempted commercially. The composition of a sample of press cake after extraction of oil from grapefruit seeds (*318*) is as follows:

Constituent	*Percent*
Moisture	3.43
Nitrogen as ammonia	4.21
Nitrogen as protein	21.60
Crude fat (ether extract)	13.95
Crude fiber	26.50
Ash	4.04
Calcium	.35
Iron	.0014
Magnesium	.39
Phosphates	.55
Silica	.081
Sodium and potassium chlorides	2.48
Sulfur	.088

The press cake is used as a protein supplement in cattle feed, but is not suitable for swine (*131*). It is toxic to chicks, probably because of its limonin content, but the toxic principle can be removed by solvent extraction (*99, 100*).

The expressed oil is run into tanks, where it is allowed to settle briefly, then pumped through filters and into storage tanks, where it undergoes a final settling before use. Subsequent treatment of the oil depends on the use for which it is destined. For edible purposes it is alkali refined. This treatment removes the bitter principle, probably limonin (*318*), and any free fatty acid. The losses in this step usually do not exceed 2 percent. The bland, neutral oil resulting may then be hydrogenated for use in shortening preparations or, if necessary, may be winterized if intended for a salad oil or liquid shortening. This treatment is accomplished by chilling until the higher melting glycerides crystallize and then removing them in a filter press. Crude grapefruit-seed oil will solidify around 10° to 14° F.

Crude citrus-seed oils are in general suitable for the usual nonedible uses to which semidrying oils are put. They include soap making, sulfonation and sulfation for detergents, and the preparation of fatty acid derivatives. Grapefruit-seed oil has found some commercial application in the treatment of textiles (*213*) and leather (*212*).

For the physical and chemical constants of citrus-seed oils, see page 17.

Flavonoids

The commercial production of flavonoids from citrus wastes was stimulated initially in 1936 by reports of the vitaminlike (vitamin P) activity of extracts of lemon peel presumed to contain physiologically important flavonoid compounds. Although the so-called vitamin P has lost favor as a vitamin, reports continue to suggest that it may have some important pharmacological properties. There has therefore been a small but steady production of several citrus flavonoid preparations. Citrus and other flavonoid compounds and their derivatives have been suggested as antioxidants (*356*), as dyes (*226, 465-467*), and for miscellaneous physiological applications (*420, 464, 477*). The reported effectiveness of flavonoids for frostbite (*124*) and radiation injury (*64, 115, 402, 403, 405*) remains controversial (*73, 88, 140*).

Hesperidin is the oldest commercially available flavonoid produced from citrus fruits (*192*). It is generally prepared from heavily limed, ground orange peel. At pH 11 hesperidin is soluble in aqueous solution as its yellow-colored chalcone. The lime coagulates the pec-

tic materials in the peel, and the extract containing hesperidin chalcone can be squeezed from the peel residue by powerful presses. The exudate is filtered, pumped to a glass-lined tank, and brought to pH 6 with hydrochloric acid. The acidulated solution is heated and allowed to stand overnight, during which time the chalcone is reconverted to hesperidin, which crystallizes out within a few hours at room temperature. The mother liquor is removed from the hesperidin in plate-and-frame filters and discarded, and the filter cake of hesperidin is dried in a tray drier.

Patents have been issued on processes for the preparation of hesperidin (*17*, *178*, *180*) and naringin (*16*). All processes are similar in principle to that previously described. A solvent-extraction procedure has been patented for the purification of crude flavonoid preparations (*245*).

Hesperidin methyl chalcone is also produced commercially. This yellow amorphous material is soluble and stable in aqueous solution. The unmethylated chalcone, formed by the addition of alkali to hesperidin, is water soluble, but reverts to insoluble hesperidin within a few hours at room temperature. Several patents (*185*, *186*, *216*) have been issued on processes for solubilizing flavonoids without chemical modification.

Naringin, a flavanone glycoside extracted from grapefruit peel, is used commercially to impart a bitter flavor to beverages, confections, and marmalade made from sweet oranges (*192*, *207*, *226*). It has no known therapeutic properties. Naringin has also been suggested as a raw material for the production of rhamnose, *p*-coumaric acid, phloroglucinol, and dyes (*226*, *348*).

An aqueous extract of lemon peel that is prepared in a manner to eliminate pectins and oils and is vacuum concentrated and dried is marketed under the name Lemon Peel Infusion, Dried. Another product, called Lemon Peel Extract, Dried, is prepared by drying an alcoholic extract of lemon peel. The two products are essentially the same, but the latter has more desirable physical properties (*192*). Both are prepared for pharmaceutical purposes.

Essential Oils

Since 1920 the production of citrus oils in the United States has increased to such volume that they are now exported to foreign markets. Production could be further increased if the demand justified, because processing plants do not extract the maximum amount of oil present in the fruit.

Current methods used in this country for manufacturing cold-pressed citrus oils may be divided as follows: (1) Those in which oil is recovered from the peel after extraction of the juice, (2) simultaneous extraction of juice and oil emulsion from whole fruit, and (3) removal of the oil-bearing flavedo (thin outer layer) from whole fruit by abrasion.

Most of the citrus oils are produced by the first method, and at least three types of machines are used. With one process the peel remaining after juice extraction is conveyed to tapered screw presses, in which the screws rotate in conical sections with ¼-inch perforations. As peel is fed into the machine, these revolving screws press it tighter and tighter against the perforations. This lacerates and twists the peel and causes oil to be released from the flavedo. The resulting oil-juice emulsion and particles of peel are washed away with water sprays. The macerated residual peel may be used for the production of pectin (p. 53).

The oil emulsion is next put through a revolving reel or other screening device to remove the larger particles of peel. It then goes through a high-force, disk-type centrifuge known as a sludger, which removes more particles and most of the water. The discharge from the sludger contains 15 to 30 percent of oil. The oil cream next passes through a solid-bowl centrifuge, which yields a 99-percent oil discharge. Most of the remaining water is then removed by a third continuous disk-type centrifuge (fig. 27), which yields an oil of greater than 99.9-percent purity. The oil is transferred to tin-lined or stainless-steel drums, and held in cold storage to precipitate sterols and waxes, which are separated by decantation. The decanted oil is given a final polishing by centrifugation, after which it is barreled and stored. The wax may be recovered and used as an ingredient in a compound for wax-treating fresh fruit in packinghouses.

Another machine, which simultaneously extracts juice and shaves off the flavedo, consists of two heavy rotating cylinders of stainless steel, one of which revolves against a perforated grid that presses out the juice after the cut fruit has been flattened by being passed through the rolls. This extractor is equipped with a peel shaver, which removes the thin flavedo from the flattened peel after the juice has been pressed and just before it is discharged from the machine. The shaved flavedo is finely shredded, mixed with water to form a slurry, and the oil separated as previously described.

Most of the oils produced in Florida are extracted from peel with a machine made of two closely set, heavy, stainless-steel cylinders,

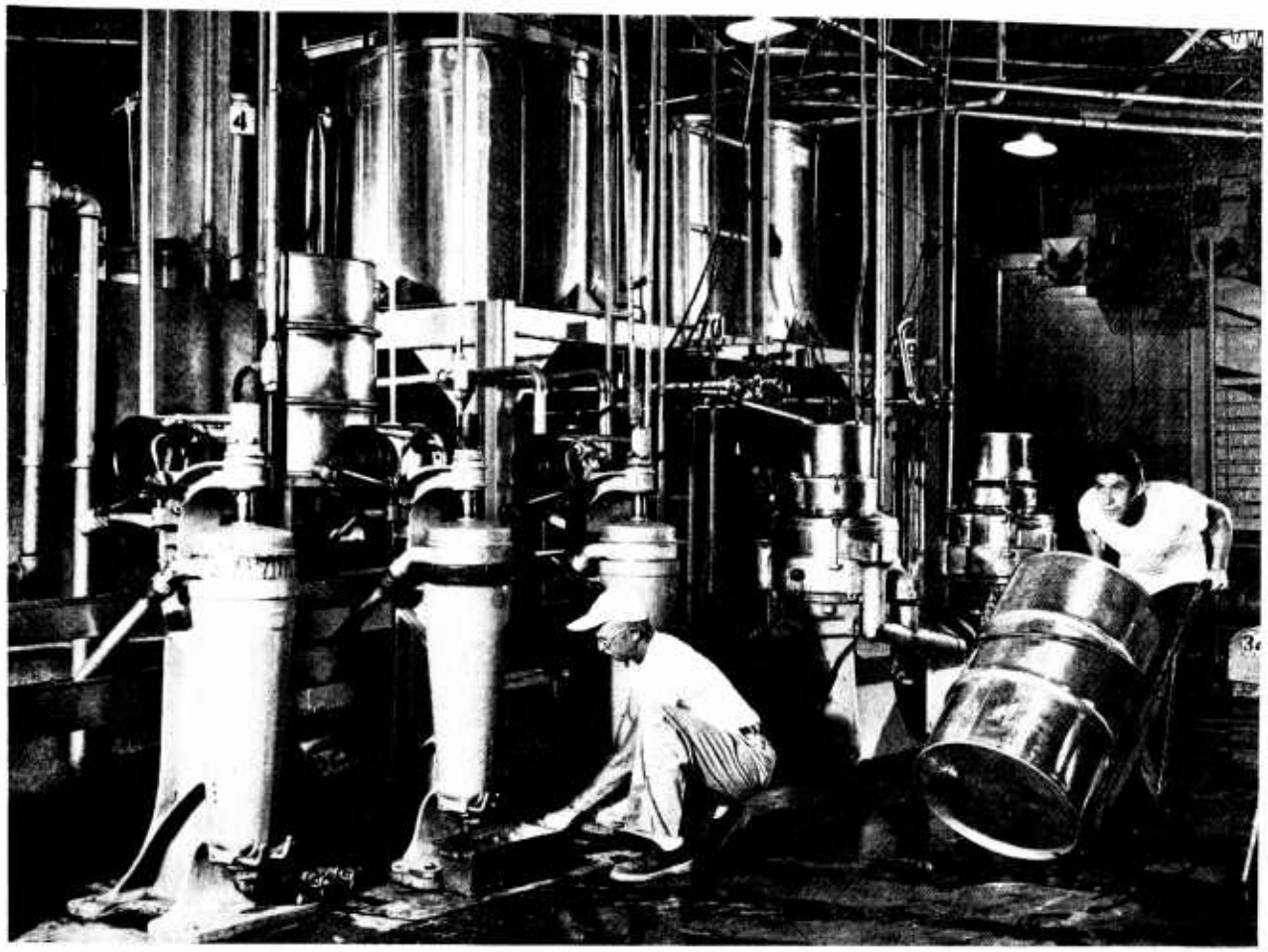


FIGURE 27.—Centrifuges used to refine citrus-oil emulsion. (Courtesy of Sunkist Growers, Inc., Los Angeles, Calif.)

which rotate slowly and are adjustable to control pressure on the peel. Sufficient pressure is maintained to just puncture the oil sacs in the flavedo without macerating the peel. The cylinders are machined with capillary grooves running around their circumference. These grooves are just deep enough to receive oil from the punctured sacs, but still keep it from being reabsorbed by the spongelike albedo of the peel as the drums revolve. As no water sprays are used, loss of water-soluble constituents is kept at a minimum. Liquid from the peel and small quantities of juice adhering to the peel act as the carrying medium for the oil. This oil emulsion is screened, and the oil separated in high-speed centrifuges as previously described.

Another method, not extensively used by the industry, consists of removing the oil-bearing flavedo from the whole fruit by abrasion. Fruit is automatically conveyed through a tunnel made up of horizontal, carborundum-covered rolls revolving at high speed. As fruit passes through this tunnel it is subjected to sufficient abrasive action to remove the flavedo to a depth of about $\frac{1}{64}$ inch. At the same time the fruit is sprayed with water, which removes the oil and peel debris as a slurry. This slurry is screened to remove solids, and oil is recovered from the emulsion as previously described. The whole fruit, minus the flavedo, is then conveyed to juice extractors. It is reported that this machine will recover more oil from a given lot of fruit than other machines used for this purpose. For example, an average yield of 9.7 pounds of orange oil per ton of peel has been reported (*227*), which is about twice the yield obtained with screw presses.

Another type of abrasive peeler used in California consists of a continuous spiral about 1 foot high, with the inner stainless-steel surface partially punched with holes to form a sharp grating surface. The spiral grater, which is stationary, is suspended over a revolving table covered with the same grating surface as the spiral. Two spiral graters of the

same size are used. Whole fruit is fed into the center of one spiral and emerges from the center of the second spiral. While the fruit is being grated through the two spirals, it is continuously sprayed with water. The resulting effluent is screened, and the oil recovered by centrifugation as previously described. The whole fruit, minus the flavedo, is then conveyed to juice extractors. This machine cannot be used to recover oil from lemons because of their elongated shape.

The yield of oil obtained under commercial conditions depends on a number of factors other than the type of machine employed. Thickskin fruit yields less oil than thinskin fruit because of the tendency for the thicker spongy albedo to absorb more oil. Fruit that has stood for some time so that the peel has become flaccid yields less oil than corresponding fruit with firm peel. Actual yields of oil per ton of fruit vary from 2 to 7 pounds for lemon oil, 1 to 8 pounds for orange oil, 1 to 2 pounds for grapefruit oil, 0.1 to 0.3 pound for lime oil, and 1 to 2 pounds for tangerine oil. These yields are far short of the actual amounts present in the peel of the respective fruits.

Cold-pressed citrus oils may be concentrated by vacuum distillation to reduce their limonene content from around 90 percent to 50 percent. These oils, referred to as "fold oils," are used mainly in beverages because of their greater storage stability.

The accumulated discharges from the cold-pressed oil centrifuges contain, on an average, 0.1 percent of oil. This liquid may be steam distilled, the vapors condensed, and the condensed water and oil collected in drums, from which the oil is decanted from the top of the water layer. The peel may also be steamed distilled, after being pressed, to obtain oil. Steam-distilled citrus oils are inferior to cold-pressed oils both in flavor and in keeping qualities.

"Stripper oil" (90 percent or more of limonene) is a byproduct in the production of citrus molasses (p. 77). This oil has been used in certain plastics and in the preparation of isoprene. A patent (*380*) has been issued for its use in preparing penetrating oils.

Oil obtained in deoiling of canned single-strength orange juice (p. 27) is also of commercial importance. This product approaches cold-pressed oil in quality, and sometimes retains a yellow color. It is of better quality than distilled or "stripper oil."

Although not manufactured by the citrus industry, terpeneless and sequiterpeneless citrus oils are available for special uses. These are oils from which practically all the terpene hydrocarbons have been removed and the more flavorful oxygenated fractions are left. Methods for their preparation include vacuum distillation, solvent extraction, or a combination of the two. A chromatographic method for preparing terpeneless oils has been reported, and shows possibility for commercial adaption (*232*).

The various types of citrus oils described are widely used in the flavoring of food products, confections, beverages, and liqueurs, and for the manufacture of pharmaceuticals, soaps, perfumes, and other cosmetics. Commercial methods for the manufacture of citrus oils in the United States and other countries, preparation of modified oils, and the uses and properties of citrus oils have been described in detail (*42, 135, 192, 229*).

The composition of American citrus oils has been the subject of considerable research. Table 19 lists some of the volatile constituents found in domestic citrus oils.

TABLE 19.—*Some volatile constituents of American citrus oils* (30, 122, 312, 314, 315, 334, 357)

Constituent	Tangerine oil	Orange oil	Lemon oil	Grapefruit oil
Acetaldehyde	---	+	+	+
Acetic acid	---	+	+	+
$C_{10}H_{18}O$ Alcohol	---	+	+	---
Bisabolene	---	---	+	+
Cadinene	---	+	+	+
Capric acid	---	+	+	---
Caprylic acid	---	+	+	---
Citral	+	+	+	+
Citronellol	+	---	---	---
Decyl aldehyde	+	+	---	+
Decylic acid	---	---	---	+
Formic acid	---	+	---	---
Geraniol	---	---	+	---
Geranyl acetate	---	---	---	+
d-Limonene	+	+	+	+
Linalool	+	+	+	+
Linalyl acetate	---	---	+	+
Methyl alcohol	---	+	+	---
Methyl anthranilate	---	---	---	+
Nonyl alcohol	---	+	---	+
Octyl acetate	---	---	---	+
Octyl alcohol	---	+	---	+
Octyl aldehyde	+	---	+	+
Octylic acid	---	---	---	+
α-Pinene	---	---	+	+
β-Pinene	---	---	+	---
γ-Terpinene	---	---	+	---

The purity of citrus oils is determined by measuring their specific gravity, refractive index, optical rotation, aldehydes, and esters, and the amount of residue on evaporation (tables 20 and 21). Sometimes, however, it is extremely difficult to detect possible adulteration by

TABLE 20.—*Approximate physical constants of domestic cold-pressed citrus oils* (458)

Source	Specific gravity (25° C.)	Refractive index (n_D, 20° C.)	Optical rotation (α_D, 25° C.)	10-percent distillate		Residue on evaporation
				Refractive index (n_D, 20° C.)	Optical rotation (α_D, 25° C.)	
						Percent
Grapefruit:						
Florida	0.8508–0.8532	1.4746–1.4761	+91.19°–92.96°	1.4698–1.4712	+95.81°–98.14°	6.02–8.02
Texas, Marsh seedless	[1].856	1.4769	[1]+96.45°			
Lemon, California	.8475–.8525	1.4738–1.4749	+52.71°–70.18°	1.4726–1.4737	+46.47°–65.74°	2.01–4.52
Lime, Florida	[1].881	1.4849	[1]+40.55°			13.74
Orange:						
California	.843–.846	1.4731–1.4742	+98.33°–94.0°			3.5–5.1
California, Valencia	.8440	1.4735	+97.78°	1.4723	+99.21°	3.6
California, Washington Navel	.8445	1.4738	+96.93°	1.4724	+98.71°	4.53
Florida	.8416–.8458	1.4718–1.4734	+95.16°–97.76°	1.4703–1.4715	+96.81°–98.70°	1.07–4.93
Texas, Valencia	[1].846	1.4742	[1]+97.10°			
Tangerine, Florida	.8456	1.4734	+91.18°	1.4711	+92.68°	4.53

[1] At 20° C.

TABLE 21.—*Approximate physical characteristics of domestic steam-distilled citrus oils* (169)

Source	Specific gravity (20° C.)	Refractive index (n_D, 20° C.)	Optical rotation (α_D, 20° C.)	Aldehydes	Esters	Residue on evaporation
				Percent	*Percent*	*Percent*
California orange	[1]0.840–0.842	1.4717–1.4730	[1]+99.1°			0.4–1.0
Florida grapefruit [2]	.8415–.8439	1.4714–1.4746	+91.50°–96.50°	2.30–4.06	0.08–2.52	.19–3.66
Florida Persian lime	.8556–.8579	1.4743–1.4751	+46.84°–50.52°	1.61–2.71	2.41–3.49	.18–1.23
Florida tangerine	.8407	1.4720	+93.67°	1.24	.25	.20

[1] At 25° C.
[2] Vacuum steam distilled.

these methods alone. Only cold-pressed orange and lemon oils are listed in the United States Pharmacopoeia.

Citrus oils should be stored in well-filled bottles or cans in a cool place. The oils are subject to oxidation in the presence of moist air, during which limonene is oxidized to carvone and carveol, and isocitral in lemon oil is changed to *p*-cymene (*419*).

Citrus Vinegar

Vinegar made from citrus fruits, especially orange vinegar, has a fine flavor and would be an easily marketable product if it could compete economically with apple vinegar. As a specialty product orange vinegar is produced chiefly in countries outside the United States.

The chemical mechanisms by which citrus vinegar is made are the same as those used for other fruit vinegars. Sugars present in citrus juices are first fermented to ethanol by the action of yeasts. The alcohol is then oxidized to acetic acid by *Acetobacter* organisms.

In the United States vinegar is required by the Federal Food, Drug, and Cosmetic Act to contain not less than 4 gm. of acetic acid per 100 ml. at 68° F. The sugar content of juice from mature oranges may vary from 8 to 11 percent, with an average of around 9.5 percent. In general, any fruit containing more than 9 percent of sugar can be converted into a vinegar, which will contain more than the legal limit of 4 gm. of acetic acid per 100 ml. Since a good orange vinegar should contain approximately 5 percent of volatile acid, as acetic (50 grain), and 1 percent of fixed acid, as citric, low-sugar citrus juices should be concentrated to increase their sugar content before being converted to vinegar. Before vinegar is manufactured from citrus juices, the regulations of the Alcohol and Tobacco Tax Division, Internal Revenue Service, covering this subject should be consulted.

Vinegar can be made from citrus juices by two methods—a slow or so-called roller process and a rapid or generator process.

The roller process is a modification of an old

French method called the Orleans process. A suitable generator consists of a 50-gallon oak barrel, fitted with a wood rack the full length of the barrel about 5 inches below the bung, which is filled with beechwood shavings or corncobs. A sufficient number of holes are bored at each end of the barrel just below the rack to allow a free flow of air. The shavings or corncobs provide a greatly increased exposed surface to bring the alcohol in closer contact with atmospheric oxygen.

If the generator is new or has not been used for some time, it should be steam scalded or thoroughly washed with hot water. After all water has been drained out, the inside of the barrel and the shavings are wetted with unpasteurized vinegar of good quality. This is the source of the *Acetobacter* organisms.

The orange juice is first fermented in a separate container by adding 1 pint of brewer's or baker's yeast to 40 gallons of juice or by using 6 cakes of compressed yeast that have been softened in orange juice. Active dry yeast, which is sold in envelopes holding 7 gm., may also be used. After fermentation has ceased, usually in 3 to 5 days, the juice is strained to remove all the yeast. The temperature of fermentation should not be higher than 85° F.

Approximately 40 gallons of this fermented orange juice is poured into the generator through the bung, which is then closed, and the holes at each end are plugged with cotton. Several times, but at least once each day, the cotton plugs are replaced with wood plugs, the barrel is turned, so the bung is at the bottom, and shaken several times to bring the juice in contact with the shavings or cobs. After the barrel is returned to its original position, the cotton plugs are reinserted. An excellent vinegar is produced by repeating this treatment daily for 60 to 90 days at temperatures around 80° to 85° F.

The rapid generator or German process allows the fermented juice to trickle down through a tall wood tank or series of tanks loosely packed with pumice, beechwood shavings, or corncobs, and thus is a continuous process (*58, 332, 336*). The pumice, shavings, or corncobs are raised off the bottom of the generator by means of a false wood bottom perforated with holes to allow a free flow of air. A similar perforated wood disk is placed on the top of the pumice or shavings.

The generator is first seeded with acetic acid bacteria by trickling warm unpasteurized vinegar through the pumice or shavings bed until it flows out at the bottom. Filtered fermented juice is then evenly distributed over the top disk and allowed to trickle down through the packed generator. A little experimenting with the air supply and flow of juice will soon establish the proper amount of air and feed to obtain efficient operation. The temperature should be kept between 80° and 85° F., and any deviation can be corrected by increasing or decreasing the flow of juice. The vinegar drawn off at the bottom will not be completely acidified, and it must be recirculated through the same generator or another generator prepared in the same manner as the first.

Orange vinegar produced by this process should be aged, which may require a year. It should then be filtered, filled at 140° F. into sterile bottles, capped, and pasteurized at 140° to 150° for about 30 minutes. The bottles are allowed to cool in air.

Care should be taken to avoid all contact with corrosive metals, such as iron, which in combination with tannins may form a black color rendering the vinegar unsalable.

The appropriate food regulatory authorities should be consulted relative to the proper labeling of orange vinegar.

Marmalades

Some dictionaries define marmalade as a preserve made by boiling the pulp of bitter or acid fruits with sugar to the consistency of jam. Modern usage usually limits the term to a citrus-fruit jelly, in which sliced or chopped portions of the peel are embedded. Federal grades and standards for orange marmalade have been established (*442*).

In making marmalade the ingredients are concentrated by cooking to such a point that the soluble-solids content of the finished marmalade is not less than 68 percent. Marmalade containing sweet orange should be composed of not less than 30 parts by weight of fruit to 70 parts by weight of sugar, whereas bitter orange marmalade should contain not less than 25 parts of fruit to 75 parts of sugar (*442*).

Marmalades contain peel in amount and physical condition according to the desire of the manufacturer. Published formulas (*55, p. 105; 75, p. 398*) call for as little as 1 pound of peel to 20 pounds of fruit pulp in tangerine marmalade and for as much as 1 pound of peel to 9 pounds of fruit pulp in sweet orange marmalade. Grade standards specify only that the peel be evenly distributed, of uniform size, and in substantial but not excessive amount. Fancy marmalades contain sliced peel $\frac{1}{32}$ to $\frac{1}{16}$ inch thick or peel chopped to small fairly uniform size.

Peel may be separated from the fruit either by reaming the juice and removing the adhering rag or by peeling the whole fruit. A con-

venient method of peeling is to heat the whole fruit for 1 to 3 minutes in boiling water to puff the peel, score it in 3 or 4 places, then pull it off by hand. Peel so obtained should be quickly and thoroughly cooled in water to prevent development of excessive toughness. It may be cooked in water to tenderness either before or after slicing or chopping. It is important that peel be completely tenderized prior to final processing, as cooking with sugar does not increase tenderness. The time required for cooking to tenderness depends on the condition of the peel, and may vary from 3 to 30 minutes at a full boil. Upon reaching the desired texture, the peel should be quickly cooled to prevent mushiness.

Sometimes cooking the peel in water serves another purpose in addition to tenderizing it. Marmalades containing two or more kinds of citrus fruit, such as orange and grapefruit, have a more appealing taste than those containing single varieties, but it is often considered advisable to reduce the bitterness of the grapefruit peel by cooking in 2 or 3 changes of water. Other strongly flavored citrus varieties, such as tangerines and calamondins, are also improved by this method of reducing flavor intensity.

Most British marmalades contain all the interior fruit juice and tissue and are semitranslucent or opaque, whereas American preference is for peel suspended in a clear jelly. The former type is prepared by cooking the peeled fruit in a small amount of water, removing the seed and undisintegrated membrane with a brush-type finisher, and adjusting the acidity with lemon juice or citric acid to pH 3.0-3.4. After the tenderized peel is added, the mixture is converted into marmalade by further cooking with sugar. Marmalades prepared in this manner, unless made from very ripe fruit, do not require the use of added pectin.

Clear-type marmalades are usually made from reamed or pressed juice. Complete clarity of the juice is not essential, as its normal cloudiness disappears upon the addition of sugar. Passing the juice through a fine mesh screen and then straining through muslin will provide the base for a very clear jelly. The use of such juice will require the addition of pectin to obtain jelly of the proper strength. Although the natural pectin content of the fruit is thus wasted, commercial manufacturers consider that the small cost of prepared pectin is little enough to pay for insurance that each batch will turn out to be of the proper consistency. Variations in the pectin content of citrus fruits are so great that laboratory tests to determine proper proportions of fruit and sugar must be run on each batch when the natural pectin content of the fruit is utilized.

For either cloudy or clear marmalade the jelly base or juice should be adjusted to the proper pH (3.0-3.4) and combined with the peel before sugar is added. An advantage from having the acid present during cooking is that some inversion of sugar takes place, which reduces the possibility of sugar crystallization. When commercial pectin is used, it is generally mixed with a small amount of sugar and added slowly with vigorous stirring to the hot but not boiling mixture. Addition of the total required sugar in small lots permits better penetration of sugar into the peel than if the whole amount is added at once. After all sugar is added, boiling is continued until the proper concentration is reached, which may best be determined by a refractometer but may be approximated by finishing at a temperature of 222° F. at sea level.

After boiling is completed, the marmalade should be allowed to stand until it cools to approximately 185° F. for skimming. Containers should be filled and sealed hot and inverted to sterilize the lids. If peel has been properly tenderized and is present in sufficient quantity, it should have no tendency to separate or float. If floating is apparent, the fault may be remedied by inverting the containers several times while cooling.

Several methods are available for preserving citrus pulp for subsequent conversion into marmalade. Much of the British production of marmalade is from imported pulp preserved with sulfur dioxide. After the cooked, sliced peel is combined with the screened pulp, the mixture is partially cooled and filled into barrels with enough sulfur dioxide solution to provide about 2,000 p. p. m. of sulfur dioxide after thorough mixing. Such a mixture may also be preserved by sealing it hot in tin cans (*384*) or by holding it under refrigeration.

Several methods for dehydrating citrus for use in marmalades have been developed. Thin slices of oranges may be dehydrated at 150° F. on monel screen trays until the fruit is brittle. This reduces the fresh fruit to 20 percent of its original weight, and marmalade prepared from such a dehydrated product is considered satisfactory (*76*).

Another method involves comminuting citrus fruit, adjusting to a pH of 2.5 to 4.5, spreading in thin layers, and drying at a low temperature (*374*).

Orange concentrate has been suggested for making marmalade (*386*). It is claimed that such a product has a vitamin C content of 17.5 to 29.2 mg. per 100 gm., or a retention of 80 percent of the original vitamin content. Com-

mercial orange marmalades generally contain 2.1 to 6.3 mg. of ascorbic acid per 100 gm. (*386*).

Brined Citrus

GRAPEFRUIT, LEMON, AND ORANGE PEEL

The peel of each of these fruits is preserved in brine and subsequently used in the preparation of candied products and mincemeat. The brining technique has long been an established practice on the Continent, but is a comparatively new industry in the United States. In the citrus regions of Italy lemons are halved and the pulp scooped out, the cleaned peels then being placed in brine. The brine is usually sea water, and salt is added to raise its density to 7° Baumé. The material remains in this solution for 4 or 5 days, and is then removed and packed in casks. The halves are packed one within another in layers, and salt is sprinkled between every second layer. The cask is then filled with 10°-Baumé brine, and the material stored for 2 months before shipment. Fresh brine is added from time to time during the storage period to keep the volume constant and the peel covered. Before shipment the brine is drawn off and replaced with sea water or its equivalent.

Sometimes the halved fruit is packed with the pulp intact (called "salati ordinari"), but a stronger brine is used than when the cleaned halves are packed, and the product is shipped at once.

Peel from which the oil has been wholly or partly removed is not considered suitable for brined peel.

In the brining of peel it is desirable to select material free from scale or melanose. The fruit used is generally the "cups" left after reaming to obtain juice for canning. The cups thus obtained still retain considerable quantities of rag, and this must be removed by hand if cleaned cups are to be brined. It is claimed (*373*) that there is now a machine available to accomplish this, and that it is being used by a concern in southern California. Cleaned cups yield a cleaner looking product than those containing rag.

The cleaned cups should be washed with water, and then packed into tight 52-gallon fir barrels, which are paraffin lined and from which the head has been removed. The cups are packed one inside the other, i.e., nested, and in rows starting at the outer periphery of the barrel. The peel should be completely covered with a 10-percent salt solution. The material is then allowed to stand until curing is completed. It is necessary to maintain the brine at 10-percent salt content by the addition of dry salt. Complete curing is judged by the appearance of the peel, which should be translucent but not mealy or mushy. Greater turgidity can be imparted to the peel by adding small amounts of calcium hydroxide, about ½ ounce per gallon of brine.

After the peel has been cured, the brine is drawn off and fresh 15-percent brine added. The barrel is headed up and stored for shipment. Stored barrels should be inspected frequently, and fresh 15-percent brine added through the bung to maintain full volume. Sulfur dioxide is sometimes added to give from 500 to 600 p. p. m. Addition of sulfur dioxide must be declared on the label of the barrel.

LIMES

Pickled limes were formerly rather popular in the Northeastern United States, especially at beach resorts where they could be seen displayed in fancy glass jars. The fruit used was the small Key or West Indian lime.

The following method of preparing this type of product is offered as a suggestion for further experimentation. The fruit should be yellow, because in that stage the peel is more tender. Green-colored fruit will sometimes become yellow or olive green when brined, but the product is not so tender as the yellow fruit. The whole fruit is gently boiled for 15 minutes in water containing 0.5 percent of sodium carbonate to remove part of the bitterness. It is then washed in clean cold water.

The limes thus prepared are placed in barrels or other suitable containers and covered with 10-percent brine. To keep the fruit submerged, it is necessary to weight it down with a lattice frame that will fit inside the barrel. The strength of the brine should be closely checked and maintained at a concentration of between 10 and 15 percent. If more salt is necessary, it may be sprinkled on the lattice so that it will not fall to the bottom of the container and remain undissolved. A scum of wild yeast and mold may form on the surface of the brine, and this should be removed by skimming; otherwise the acidity of the brine will be reduced.

The temperature during curing should be between 80° and 85° F. At the end of 30 days the brine should be discarded and fresh brine added. The finished product should not be mealy; if mealy, it indicates improper curing.

At the end of the curing period the brine is discarded and the fruit processed by covering with water and maintaining at 120° F. for 3 to 4 hours. The limes are then removed from the water, rinsed, packed into the final container,

and covered with 5-percent brine to which vinegar has been added to bring the acidity to 2 percent. If a more sour product is desired, the acidity may be increased to 4 percent.

CITRON

For commercial purposes citron (*Citrus medica*) 5 or 6 inches long and 3 or 4 inches in diameter is generally used. It should be picked green but full grown. Yellow well-ripened fruit is not suitable for brining. Satisfactory fruit will exhibit a certain oiliness on the surface, and the oil sacs will be well developed.

The washed fruit is cut in half lengthwise, but the seeds and pulp generally are not removed. It is packed into crocks or barrels and covered with brine. The brine may be either natural or artificial sea water of the following approximate composition:

Sodium chloride	28 pounds
Potassium chloride	7 pounds
Magnesium chloride	3 pounds
Water	100 gallons

If curing temperatures run higher than 60° F., salt must be added to raise the concentration to 7-10 percent.

During brining the tissues of the fruit become translucent, and a vigorous growth of yeast takes place. The length of time for curing will vary with the size of the fruit, its maturity, and temperature during curing. In general, the period varies from 16 to 30 days. During brining it is necessary to keep the solution at the proper strength by the addition of salt. After curing is completed, the brine is removed and replaced with a 6- to 10-percent salt solution.

Candied Citrus

GRAPEFRUIT, LEMON, AND ORANGE PEEL

The raw material used for candying the peels of these fruits (*37, 57, 106*) may be either fresh or brined. However, brine must be removed by soaking the peel in cold or hot water. Peel for candying should be free of blemishes and reasonably thick. The flavedo, or oil-bearing surface, should be scoured with a wire brush or roughened with a cheese grater in order to release part of the peel oil. Adhering membrane should be removed from the peel, which should then be cooked until tender. As many changes of water should be used in cooking as considered necessary to reduce the strong flavor of the peel. Grapefruit peel is normally quite bitter, and several changes of water are required to reduce the bitterness to an acceptable level. However, all bitterness should not be removed, as it is a distinguishing characteristic of the fruit. Nonbitter candied peel may be prepared from oranges or lemons. After the peel is cooked, it should be drained and pressed as dry as possible. Although it may be cut into strips or pieces as desired before cooking, circulation and drainage of hot water are more rapid and handling is easier if half or quarter peels are used.

Since the peel of juice types of citrus is more porous than citron, sugar will saturate it, so that the tedious process required for citron will not be necessary. The tenderized peel may be boiled slowly for about an hour in a sugar solution consisting of equal parts of sugar and water and 0.05 percent of citric acid. The peel is allowed to remain in this solution overnight. It is then boiled again until the temperature reaches 219° F., and drained while still hot. Overcooking should be avoided to prevent hardness in the finished product. Stickiness may be reduced by dipping the hot peel quickly into boiling water, draining, and drying on wire trays in a current of warm air. Dusting with powdered sugar prior to complete dryness will also tend to keep the pieces from sticking together. Candied peel should be stored in moistureproof containers.

KUMQUATS

Kumquats are grown extensively in China and Japan. The fruit is also grown in Florida, where the Nagami (*Fortunella margarita*) and the Marumi (*F. japonica*) species are found. The plant is a shrub, reaching a height of 10 to 15 feet. Its fruit is oblong in shape, varying from 1½ to 1¾ inches in length. It is much used for holiday decorative packing, being harvested along with a few branches and leaves. The bright-orange outer rind has a spicy flavor, the inner rind is sweet and granular, and the juice has an acid taste.

Kumquats are consumed chiefly after being candied. Considerable difficulty is experienced in candying them, because the fruit generally collapses and the product does not have a pleasing appearance.

The fruit is first washed and then passed on a belt beneath a spiked roll to puncture the peel. The belt can be either leather, rubber, or stitched canvas, through which copper tacks are driven and held in place with a suitable backing. The roll and belt should be so adjusted that the fruit is not torn or impaled on the spikes.

After the fruit is punctured, it is gently boiled in water for about 30 minutes, but the time of boiling will depend on the condition of

the fruit. Boiling should not be so prolonged that the fruit disintegrates, but merely sufficient to render the kumquat tender. The fruit is then drained and boiled for 30 minutes in a 20-percent sugar sirup. Additional sugar is added to increase the sugar content to 40 percent and boiling continued for another 30 minutes. It is then allowed to remain in this solution overnight. The next day sufficient sugar is added to increase the sucrose content to 55 percent, and the fruit is boiled for 1 hour and allowed to remain in this sirup overnight. It is then drained and any collapsed fruit is culled. The remaining fruit is packed into jars and covered with boiling 60-percent sirup. The jars are sealed and allowed to cool in air, and no further processing is necessary.

CITRON PEEL

Brined citron should be boiled in several changes of water until tender, or until a needle will easily penetrate. The boiling time can be reduced by cutting the peel into small pieces of the desired shape. Both salt and sulfur dioxide are substantially removed in this tenderizing process. To restore crispness the freshened peel should be soaked in cold water.

Sirup used in candying must contain some invert sugar in order to prevent crystallization of sugar in the finished product. The original sirup may be made up to contain either 60 percent of sucrose and 40 percent of dextrose, or corn sirup, or all sucrose plus approximately 0.05 percent of citric acid. Candying procedures vary, but all consist of heating the cured citron in increasingly concentrated sirups over an extended period of time.

The following procedure has been found to produce an attractive stable product. Prepare a 20-percent sirup, heat to boiling, and add the tenderized peel. Set aside overnight. Add 1 pound of sugar for each pound used in the original sirup, reheat to boiling, and set aside overnight. Repeat this procedure until 4 pounds of sugar have been added for each pound used originally. After the peel has set overnight in the final sirup, remove and drain the peel, then dip quickly into boiling water twice, and dry the pieces on wire trays under a current of warm air.

For use in baking, the candied citron may be stored indefinitely in sealed containers without further treatment. For use as a confection, the pieces may be rolled in powdered sugar while still damp, or they may be glazed by dipping in a hot saturated sugar solution containing 3 parts of sucrose to 1 part of corn sirup, draining, and drying in a current of warm air.

WASTE DISPOSAL

Dilute Liquid Waste

Great strides toward the elimination of wastes created during citrus processing have been made by utilizing some of the solid and concentrated wastes for feed and molasses manufacture (p. 73). However, there remains the problem of disposing of large volumes of process water containing small amounts of citrus juice.

When the processing plants were small, their dilute waste could be dumped into streams, lakes, or tide waters without upsetting the biological balance of the receiving waters. However, citrus processing has become a major industry, and organic solids carried by dilute waste are now calculated in tons rather than in pounds. When these materials decompose, oxygen in the water is used up, fish and plants die, and anaerobic or putrefactive reactions set in with the consequent creation of a major nuisance.

Factors affecting the magnitude of the waste-disposal problem for each plant include the size of the plant, the products being manufactured, and the efficiency of plant sanitation. Large plants, of course, use more water, most of which becomes contaminated to some extent. Plants producing single-strength juices use large quantities of water to wash the incoming fruit, to cool the canned juices, and to wash processing equipment. Plants canning fruit sections use water for the same purposes, and in addition use hot lye on the peeled fruit and copious quantities of fresh water to rinse off the lye solution. Concentrate plants must exercise greater sanitary precautions because their product is unpasteurized, and they must continuously use large amounts of chlorinated water to keep conveyors and fruit clean. They also use large quantities of water in their vapor condensers. Surface condenser water may not become contaminated, but barometric condenser water contains some peel oil and picks up a trace of juice by entrainment. Plants manufacturing citrus pulp and molasses may have wastes very high in organic material, although the volume should be much lower than that from food-processing plants. Effluents from peel-oil mills are high in organic materials and are very difficult to treat.

Waste waters can be grouped roughly into three classes according to their soluble-solids content. First, there is the very dilute waste containing little more than a trace of organic matter, such as fruit-rinsing water, surface condenser water, and water from barometric condensers of evaporators. Usually these

waters can be discharged directly into lakes, streams, or bays without ill effect.[6] Next comes the waste of intermediate concentration, such as floor washings, equipment cleanup water, and sectionizing waste. These waters range from a trace to about 2 percent in soluble solids, and need some treatment unless the receiving body of water is exceptionally well situated. The third classification ranges roughly from 2 percent to 6 percent in soluble solids, and includes drippings from can-closing and filling machines, effluent from peel-oil centrifugals, and waste alkali from sectionizing or evaporator cleaning. This waste generally requires treatment of some kind. With the exception of waste alkali, this waste is such that concentration into molasses may be considered as a method of treatment.

FIGURE 28.—Lagooning of liquid citrus waste.

METHODS FOR DISPOSAL

The organic matter of dilute citrus waste is high in carbohydrates and low in nitrogen in contrast to domestic sewage, which is low in carbohydrates and high in nitrogen. Methods commonly used for the treatment of domestic sewage are, therefore, not adaptable without modification for treatment of citrus waste. Wastes from a small processing plant and from a fairly large city might profitably be treated together (*3*), since the combined wastes would have all the nutrients needed for rapid microbial action and consequent reduction of the biochemical oxygen demand (B. O. D.). A disadvantage to such a plan is that citrus processing is seasonal, and the peak of the season coincides with an annual influx of winter visitors. These circumstances necessitate the installation of oversize treatment plants at considerable cost. Processing plants have sometimes been called on to bear a major share of the cost of such plants.

Plants located near large areas of deep sand, away from population centers, are fortunate in having an inexpensive and satisfactory means of disposal at hand. Dilute waste may be conducted into a series of basins, where the liquid percolates into the soil and solids are dried by the sun. Sufficient land must be available to permit rotation of disposal areas so that surfaces which become clogged may be allowed to dry and may be cultivated for renewal of their absorptive capacity (*199*). One large plant in California (*255*) has used this method for a number of years. Some income is derived by periodically withholding treatment from a portion of the disposal area and by using it to produce farm crops.

Spray irrigation of pasture and wooded land in Florida with citrus waste (*3, 324*) proved destructive to vegetation, but might prove successful if the waste were applied less heavily on pasture land bearing a leguminous cover crop (*376*).

Pumping waste water into wells was tried in Florida and in Texas, but was abandoned because of contamination of underground water supplies. Excessive pressures were developed by anaerobic fermentation, and the wells blew back, with damage from ensuing fire in at least two instances (*267*).

The lagooning of wastes (fig. 28) has been tried for a wide variety of cannery effluents. Only under very special conditions has this method met with success. Unless expensively treated with supplemental nitrogen, extensive aeration, and chemical flocculation, lagoons soon became offensive (*199, 267, 375, 457*).

Chemical flocculation and precipitation of rather heavily contaminated cannery effluents have been attempted, but have not shown sufficient merit to warrant widespread use. In Texas several thousand tests with lime and alum as precipitants indicated an average reduction of 30 percent in B. O. D. (*431*). In Florida the addition of lime for flocculation, with aeration to promote floating of solids, resulted in a 64-percent reduction in suspended solids (*3, 324, 463*). Ground phosphate rock has also been used to promote flocculation. Although chemical flocculation can be accomplished at small expense for personnel and equipment, the cost of chemicals is high. Such treatment does not significantly reduce the oxygen demand of the wastes, but is helpful in regulating the pH and clarifying the wastes for subsequent treatment.

[6] Under no circumstances can effluents from canneries or retention tanks be discharged into a stream without permission from the proper Federal, State, or local authorities.

BIOLOGICAL TREATMENTS

An important factor contributing to the difficulty of biological treatment is the seasonal and sometimes intermittent supply of citrus waste. Biological filters and digesters rely for proper operation on a continuous feed supply of fairly uniform composition. Biological treatments investigated include simple yeast fermentation, methane production, trickling filters, and an activated sludge process.

Aerated fermentation by yeast is a simple and rapid method of removing from dilute citrus waste the sugars, which comprise about two-thirds of the organic matter present. This procedure was demonstrated in experiments on the production of feed yeast (p. 78). Remaining decomposable organic matter includes alcohols, esters, pectins, pectin-degradation products, glycosides, and salts of citric acid (*450*). Application of yeast fermentation has been made as a preliminary step in methane fermentation and in activated sludge digestion.

Methane production from fairly concentrated citrus waste has been extensively investigated (*268-270*). Substrates were diluted orange juice and effluent from a peel-oil mill. Initial production of methane was satisfactory, but progressive inhibition of fermentation occurred. It was found that citrus-peel oil contributed the inhibiting factor. Even when a substrate was prepared from citrus molasses from which peel oil had presumably been removed during evaporation, there remained a decidedly inhibitory effect. Complete removal of peel oil was accomplished by a preliminary treatment of the waste, consisting of aerobic yeast fermentation with vigorous aeration (*270, 484*). Waste containing at least 0.5 percent of solids is needed for satisfactory digestion. With waste containing less than 1 percent of solids, lime must be used to maintain a pH around 7, and nitrogen must be added as a supplemental nutrient. The principal difficulty is in retaining sufficient bacterial sludge in the digester. Complicated sludge manipulation and the preliminary aerobic treatment make the value of the process rather limited (*269*).

Biological oxidation of citrus waste on trickling filters has been extensively considered. The earliest reported pilot-plant investigations (*461*) indicated that trickling filters could be used to eliminate up to 80 percent of the oxygen demand if the weather remained warm. Later investigations (*324, 431, 463*) showed that with a high ratio of recirculation (6:1 to 8:1) and added nutrients (50 p. p. m. of nitrogen and 20 p. p. m. of phosphates) it is possible to operate trickling filters on citrus waste having a B. O. D. as high as 2,000 p. p. m. and to produce an effluent with a B. O. D. of less than 500 p. p. m. The chief difficulty in maintaining filter efficiency was due to the intermittent incorporation of strong alkali (used to clean evaporators and juice lines) in the waste waters, with resulting destruction of biological growth on the filters. It has been demonstrated (*230*) that segregation of alkaline wash water for use in citrus-pulp manufacture is economically advantageous. Removal of this adverse factor would make trickling-filter operation feasible.

The biological disposal method that has received rather widespread attention is an activated-sludge treatment. The primary reason for failure of early activated-sludge experiments was the low nitrogen content of citrus waste. A series of experiments at the Southwest Foundation for Research and Education, San Antonio, Tex., showed that it may be possible to operate an activated-sludge system without adding chemical nitrogen (*266*). Under certain conditions nitrogen bacteria when inoculated into activated sludge continue to propagate and supply sufficient nitrogen to permit digestion in a 23-hour cycle to the extent of 99.9-percent reduction of B. O. D. of orange juice diluted 1:49.

Investigations by the Texas State Department of Health have shown that an activated-sludge pilot plant could be operated successfully on wastes from both citrus- and tomato-canning plants (*378*). This plant operated in three stages—8 hours' storage, 8 hours' aeration, and 3 hours' final settling. The 8 hours of storage, in which fermentation was started with brewer's yeast, was necessary to condition the citrus waste for digestion in the second stage by organisms originally obtained from a municipal activated-sludge plant. Part of the sludge from the settling tank was returned to the aeration tank and the balance discharged. When dilute waste with a B. O. D. of less than 1,000 p. p. m. was used, reductions in oxygen demand were obtained to as low as 1 p. p. m.; when waste with a B. O. D. up to 2,000 p. p. m. was used, effluents below 500 p. p. m. were obtained. No mention of the use of added nutrients was made.

In Florida, experiments (*96*) were run on orange juice diluted to a B. O. D. of about 2,000 p. p. m., with results similar to those reported above. Other experiments in Florida (*463*) indicate increased efficiency of activated-sludge treatment when 50 p. p. m. of nitrogen and 20 p. p. m. of phosphates were added as nutrients.

At least one processing plant in Florida handles its disposal problem by emphasizing in-

plant sanitation (*273, 485*). An analysis was made of each plant operation, and its contribution to waste actually measured. It was always found that waste could be reduced, and sometimes it was turned into profit. Such concentrated waste as bin drippings and cleanout water from evaporators, tanks, and homogenizers was pumped into storage tanks for conversion into feed molasses. Settling tanks were installed in condensate lines from molasses evaporators to permit recovery of distilled oil, which not only returned a profit but also removed an unexpectedly potent pollution factor. A program of employee education was instituted, emphasizing the elimination and reporting of leaks, the conservation of water, and general good housekeeping. As a result of this overall program dilute waste from the plant was being emptied directly into a salt-water bay without treatment and without creation of a nuisance.

Citrus Feed

When citrus fruits are processed for juice or sections, there remains for disposal or utilization 45 to 60 percent of their weight in the form of peel, rag, and seeds. This material was originally considered as waste, and for lack of a better name is still so called. An analysis of grapefruit cannery waste is reported in table 22.

TABLE 22.—*Analysis of grapefruit cannery waste* (335)

Constituent	Florida grapefruit		California grapefruit
	Peel	Rag	Peel and rag combined
	Percent	*Percent*	*Percent*
Total solids	16.71	15.60	22.02
Ash	.74	.75	.70
Volatile oil	.43	--------	.56
Acid, as citric	.74	.63	.43
Crude fiber	1.71	1.44	2.00
Crude protein (N×6.25)	1.13	1.06	1.63
Crude fat (ether extract)	.28	.16	.23
Total sugar (as invert)	6.35	6.30	8.68
Pentosans	.83	.44	1.31
Pectin (calcium pectate)	3.10	3.56	3.93
Naringin	.40	.10	.63

In the 1920's and early 1930's the quantity of such waste was insufficient to cause concern to the citrus-canning industry (*457, 458*). Sometimes the material was returned to groves for its fertilizer value, and disked in or covered with soil to discourage fly breeding. Soil-building value of the waste is largely limited to its humus value. Its nitrogen content (about 0.14 percent) is insufficient to support the bacterial action of decomposition, and it will therefore rob the soil of existing nitrogen unless supplemented by chemical fertilizers. One method of overcoming this deficiency was to add cyanamide to the ground material. Between 200 and 400 pounds of calcium cyanamide were added to each ton of ground waste, mixed thoroughly, and allowed to stand until the mass became dry and crumbly. There was a gradual loss of ammonia from the mixture, and no guaranteed analysis could be safely given. Sometimes nitrates, ammonium sulfate, and superphosphate were added along with the cyanamide (*217, 398*).

Feeding value of cannery waste was early recognized by dairymen and cattlemen located in the vicinity of citrus canneries (*1, 285, 353*). Because of the high water content and perishable nature of the waste, it could not be transported economically for feeding purposes. The fresh material was difficult to handle, fermented rapidly, and soured, and became a fly-breeding and odoriferous nuisance. Its preservation by ensiling has been reported (*25, 38*), but the method has not been widely adopted. Stabilization of the waste by drying seemed the logical manner for preservation to permit distribution and storage. However, direct drying could not be successfully practiced because of the high moisture content (80 to 85 percent) and the slimy consistency of the waste.

It was found that the hydrophilic nature of the pectin in the waste could be destroyed by adding lime (*67, 250*), and its moisture content reduced by draining and/or pressing. A number of patents (*48, 49, 65, 67, 243, 250-252, 309, 452-454*) covering the drying of citrus waste have been issued.

As early as 1927 orange pulp was being dried in California for use as a livestock feed. Dried grapefruit pulp was available in Florida in about 1932, and in 1938 Texas producers were shipping as far as New England. Considerable experimental work has been carried out on the feeding of dried waste to both dairy and beef cattle (*7, 69, 89, 206, 236, 285, 310, 428*). In general, it has been found to be similar in feed value to beet pulp, being low in crude protein, fiber, and fat, but high in nitrogen-free extract, or carbohydrate, which is 88 to 92 percent digestible. It is classed as a high carbohydrate

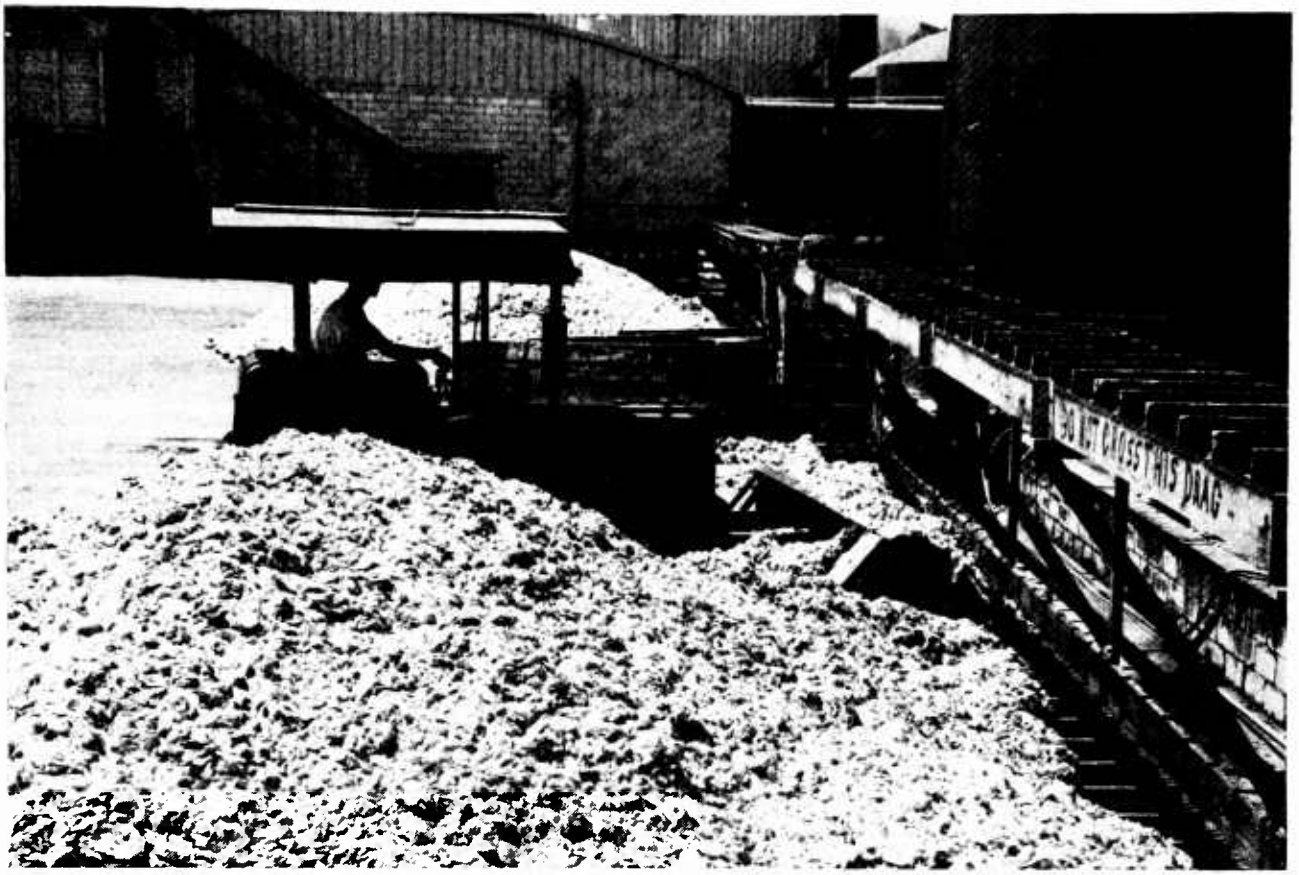


FIGURE 29.—Loading citrus waste onto a dragline for grinding and liming. (Courtesy of Florida Citrus Canners Coop., Lake Wales, Fla.)

concentrate. A typical analysis of dried citrus pulp (*169*) is as follows:

Constituent	*Percent*
Ash	4.3
Crude fat	3.5
Crude fiber	13.0
Crude protein	6.2
Dry matter	92.0
Nitrogen-free extract	63.0

Modern methods of extraction and finishing have increased juice recovery, reducing the percentage of waste in 10 years from about 65 percent of the fruit entering the processing plant to an average of less than 50 percent. Citrus waste in 1955 probably amounted to about 2 million tons, most of which was converted to cattle feed, with a production in Florida at that time of some 300,000 tons.

There is a great deal of variation in plant design and in methods used for the manufacture of cattle feed from citrus waste. Detailed descriptions of individual plants have been published elsewhere (*150, 163, 169, 192, 389*), and therefore a general description of the major processing problems will suffice here.

Figure 29 shows citrus waste being loaded onto a dragline for grinding and liming. Figure 30 shows the sequence of operation in a feed and molasses mill and gives performance examples. The peel, rag, and seeds are disintegrated in hammer mills or shredders, then 0.3 to 0.6 percent of lime is added, either dry or as a slurry. Sometimes the lime is added before or during shredding. Some operators add lime at a constant rate, whereas others vary its addition according to color changes or the pH of the aging mixture.

Pug mills, which in their simplest form are large screw conveyors with flights interrupted to promote mixing, are used for rapid curing. Constant agitation and remixing of the pulp and released liquor provide intimate and renewed contact between reacting constituents. When bins are used, a minimum of ½ hour is required for curing.

After proper curing the waste is in satisfactory condition to be pressed. Pressing is facilitated if the material is heated. Continuous presses are used to reduce the moisture content from 81-83 percent to 70-75 percent, during

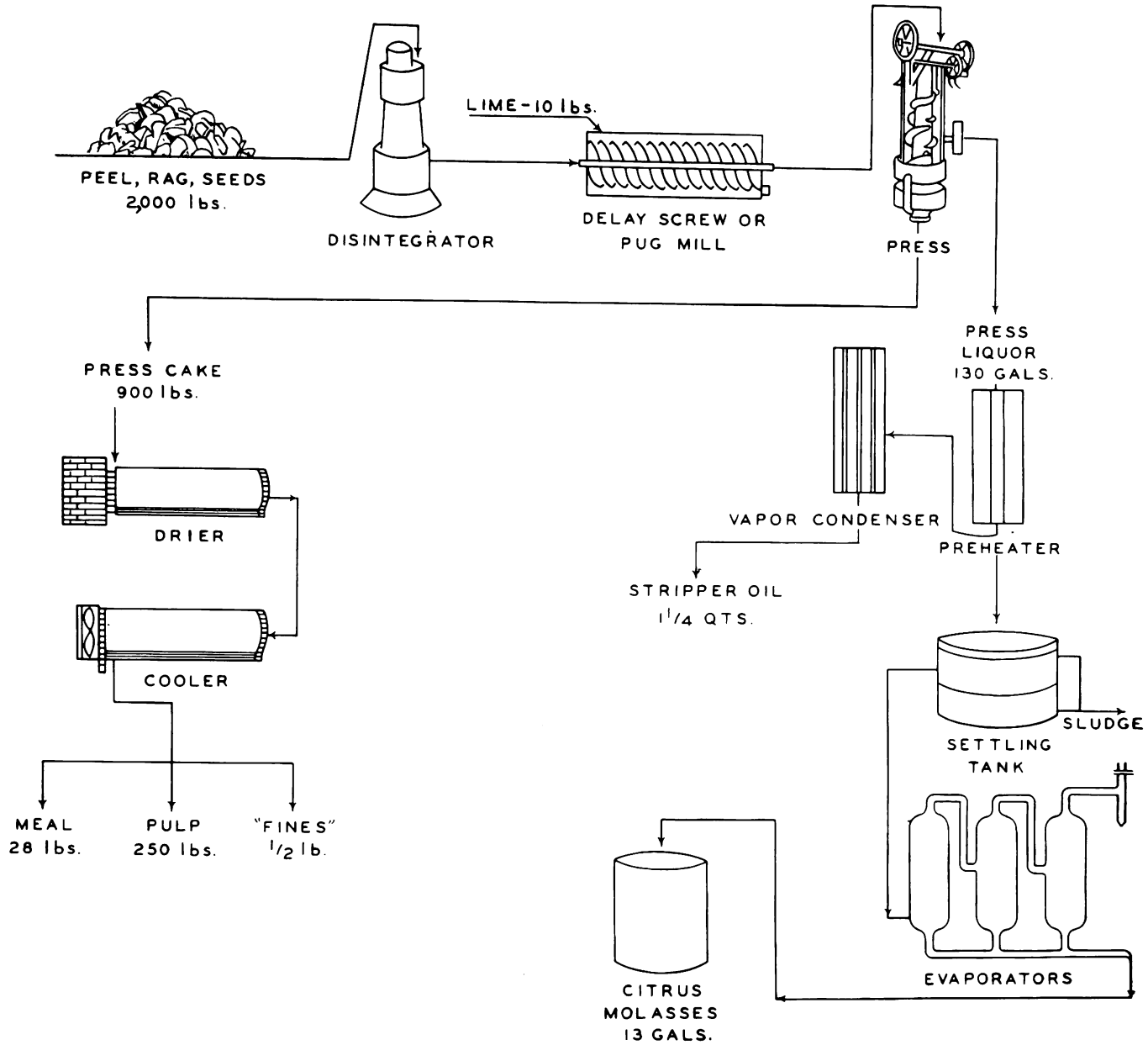


FIGURE 30.—Flowsheet showing steps in the production of citrus feed and citrus molasses.

which operation more than half of the original weight of the waste is removed in the form of press liquor containing 10 to 15 percent of dissolved solids. Treatment of the press liquor is discussed on page 77. After the material is dewatered, either by drainage or pressing, it is ready for drying.

A single-shell, direct-fired rotary kiln is the simplest form of drier (fig. 31). Cured waste, obtained as described, is dropped into a blast of air and furnace gases at the end of the kiln next to the firebox, and is lifted and dropped repeatedly through the hot air stream by staggered oblique vanes attached to the inside of the rotating kiln. Progress of the feed through the kiln is enforced by proper placement of the vanes. Also as the material dries and becomes lighter, it becomes more susceptible to the action of the air draft induced by suction fans, and the very small pieces, which dry first, are drawn out and collected in a cyclone separator. This material, called "fines," is sold as a fertilizer extender. The heavier pulp leaves the kiln at temperatures above 200° F., and is cooled by

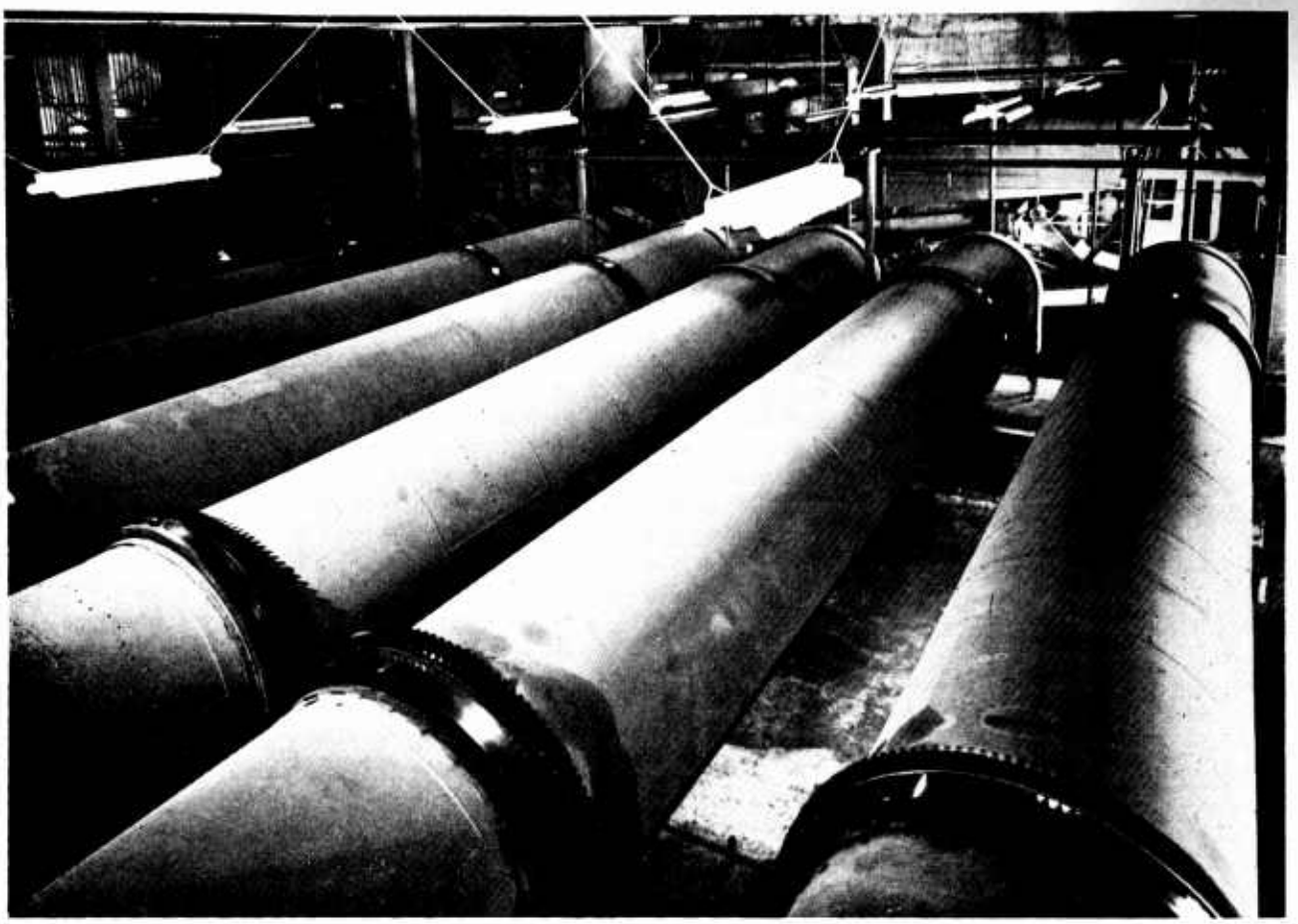


FIGURE 31.—Rotary driers for making citrus waste into feed. (Courtesy of Florida Citrus Canners Coop., Lake Wales, Fla.)

being dropped through a current of fresh air in a rotating unheated cooler. The last few feet of the cooling cylinder may be composed of wire netting, which screens out the smaller pulp pieces. This material, called "meal," is bagged separately and sold for mixing in prepared feeds, or may be pelleted for range feeding. Fines and meal amount to less than 10 percent of feed-mill production.

Some of the larger plants having several kilns group them and use a 2-stage process. Several kilns at high temperatures can be used for primary driers, reducing the moisture content of the pulp to 35-40 percent. Combined output of 3 or 4 primary driers can be finished to 10-percent or lower moisture in a single secondary kiln maintained at lower temperatures. Heavier loading of the secondary kiln with a lower ratio of air to product is possible, because surface moisture of the pulp has already been removed and drying can be no faster than the rate of migration of the moisture from inside the pulp pieces. Air warmed sufficiently to maintain an outlet temperature of 210° to 230° F. serves to remove moisture vapor as fast as it is released, and is not hot enough to cause scorching of the product.

Variations in design of direct-fired driers include single-shell kilns 4 to 6 feet in diameter and 30 to 60 feet long and double- or triple-pass kilns, which have concentric cylinders with the product passing first through the center of the smaller cylinder and then consecutively through the annular spaces between them. Steam tube driers produce minimum heat damage to the product, but they remove moisture so slowly that multiple units are usually required and the investment in equipment is extensive. For good economy, exhaust steam should be used to heat the driers.

Pressing of cured pulp is generally practiced in Florida because of high fuel costs, but in Texas cheap fuel is available and pressing has been omitted. During aging in bins, where free drainage of released moisture occurs, the moisture content is reduced by only about 2 percent.

Drying kilns handling unpressed cured waste must evaporate more than twice as much water per unit of waste as those handling press cake (*163*). Cost of kilns to provide extra capacity is less than the cost of presses and multiple-effect evaporators required to handle large amounts of press liquor. The lower efficiency of fuel utilization in kilns as compared with that in multiple-effect evaporators should be studied before the type of operation is finally determined.

Some plants in Florida eliminate the need for pressing by returning partially dried feed to the pug mill to absorb moisture as it is released from freshly limed and ground peel. Such a scheme of operation results in eliminating the problem of disposition of the press juice and drainage liquors. Plants allowing free drainage from limed peel in bins must handle or dispose of drainage liquor, which amounts to as much as 20 percent of the weight of waste received (*389*). Plants using presses must handle in the form of press liquor more than half the waste received.

Manufacturers using presses may produce feed containing the full complement of carbohydrates of the whole waste by concentrating their press liquor in multiple-effect evaporators and returning it to the feed line at any one of four places: To the press cake as it enters the primary driers (*243*), to the partially dried feed between stages, to the hot dried feed, or even to the feed brought from the warehouse for mixing. Controlled tests indicate that pulp containing up to 50 percent of added molasses tends to pick up little, if any, more moisture than does dried pulp alone, when stored at a relative humidity of 70 percent or less. All samples, with or without molasses, will mold when stored at a relative humidity of 80 percent or higher (*32*).

From 8 to 12 tons of fresh waste are required to yield 1 ton of dry feed.

Citrus Molasses

Liquid obtained from cured citrus waste contains from 10 to 15 percent of soluble solids, of which from 50 to 70 percent are sugars (*322, 451*). This material, which may amount to more than half the total weight of cannery refuse available to the feed mill when presses are used, is far too valuable to discard. Furthermore, disposal itself would be rather expensive. The liquor has a B. O. D. of between 40,000 and 100,000 p. p. m. (*457*), and creates an excessive nuisance when dumped into lakes or streams. This carbohydrate-rich material may be used for making feed molasses, as it can be mixed with citrus pulp or sold separately to cattle feeders or to manufacturers of mixed feeds.

For conversion to molasses the press liquor is passed through vibrating screens to remove as much of the suspended solids as possible, then flash heated to reduce subsequent scaling in the evaporator tubes used to concentrate to 72° Brix. Scaling can be further reduced by using waste alkali from sectionizing plants and evaporator cleanup operations (*230*). If the liquor is superheated (220°-260° F.) in a tubular heat exchanger, then is flashed into a vapor-liquid separator, and the vapors are conducted to a surface condenser, an appreciable ducted to a surface condenser, an appreciable ered as a byproduct (*345*). Some clarification of the press liquor can be obtained by holding it in settling tanks after heating, then drawing off the evaporator feed material from a point below the surface and above the settled solids. The sludge, composed of both floating and settled solids, may be disposed of by spreading it on sandy soil. Heating alone apparently modifies the material so that scaling in evaporator tubes is reduced, but clarification prior to concentration gives a molasses that is better appearing, less viscous, and more stable and that has higher sugar and lower ash than molasses obtained from unclarified liquor (*167*).

Clarification has been obtained in Texas by heating with submerged combustion burners (*48, 49, 389*). In this method carbon dioxide comes into intimate contact with the liquor constituents and promotes defecation by carbonation, in addition to the effect of temperature. In practice the liquor is slightly concentrated by a submerged burner to about 15° Brix, then passed through a clarifier, or continuous settler, and into a second submerged burner, where it is further concentrated to about 22° Brix. The discharge from the second burner goes into additional settling tanks, thence to a multiple-effect evaporator.

At least one feed mill produces citrus molasses from press liquor by use of falling-film, low-temperature evaporators similar to those used for the production of frozen citrus concentrates (p. 40). With this equipment scaling of evaporator tubes is apparently not a problem. The molasses produced is light in color and, although unclarified, is not exceptionally viscous.

Citrus molasses is normally a thick viscous liquid, which is dark brown to almost black and has an extremely bitter taste. Florida standards require it to contain at least 45 percent of total sugars, as invert, and to test not less than 35.5° Brix after dilution with an equal weight of water (*169*). During storage there is a small decrease in pH and in total

sugars and a small increase in invert sugar and in viscosity (*168*).

A typical analysis of Florida citrus molasses (*169*) is as follows: It has a concentration of 72° Brix, a pH of 5, and a viscosity of 2,000 centipoises at 25° C. In addition to 35 p. p. m. of niacin, 11 p. p. m. of riboflavin, and 10 p. p. m. of pantothenic acid, its composition includes—

Constituent	*Percent*
Nitrogen-free extract	62.0
Total sugars	45.0
Moisture	29.0
Reducing sugars	23.5
Sucrose	20.5
Carbonate ash	4.7
Acid, as anhydrous citric	4.5
Nitrogen × 6.25	4.1
Glucoside	3.0
Pentosans	1.6
Pectin	1.0
Fat	.2
Volatile acids	.04
Potassium	1.1
Calcium	.8
Sodium	.3
Magnesium	.1
Iron	.08
Chlorine	.07
Phosphorus	.07
Silica	.01
Manganese	.008
Copper	.003

Citrus molasses resembles cane molasses and is similarly used for feeding both dairy and range cattle (*24, 189, 359, 360*). Its extreme bitterness makes it unsuitable for human consumption unless treated for removal of naringin (*50, 404*), but the bitterness does not affect its usefulness in cattle feeding. Citrus molasses may be admixed with pressed pulp just prior to being placed in the drying kilns, and thus the ratio of total digestible nutrients to crude fiber is increased in the dried product without destroying the keeping quality of the pulp (*32*). It may also be used in the preparation of balanced prepared rations. In Florida large quantities are fed directly to cattle from troughs supplied automatically with molasses from storage tanks. As much as 6 pounds, or 0.5 gallon, may be consumed per head per day. Citrus molasses may be used for feeding swine (*77, 78*), but is not so readily accepted by swine as by cattle.

The feeding value of citrus molasses is sometimes enhanced by ammoniation (*283, 292*) or by the addition of urea to increase the crude protein content.

Feed Yeast

Press liquor obtained during the manufacture of dried citrus pulp contains sugars available as a raw material for industrial fermentations. The production of feed yeast has been considered, because it is rich in protein and B-vitamins. Since fermentation and production of this type of yeast are very rapid, opportunities appear favorable for utilization of press liquors on a large scale.

The potential supply of fermentation sugars from such liquor is over 100 million pounds a year considering the liquor that could be made from all the fruit used in citrus-processing plants. The potential yield of dry yeast from this liquor would be about 50 million pounds.

Strains of *Torulopsis utilis* have generally been used for feed yeast, because they can be propagated on a wide variety of materials and are rapid growers.

The crude protein content of dried *Torula* yeast from citrus press liquor ranges from 45 to 55 percent (*94, 322*), and compares favorably with other proteins in digestibility. Although studies have not been conducted on the amino acids present in yeast from citrus waste, the composition of yeast from other sources will serve as a guide. *Torula* yeast has been found to contain arginine, cystine, glutamic acid, glycine, histidine, isoleucine, lysine, methionine, phenylalanine, threonine, tryptophane, tyrosine, and valine. All amino acids that have been found indispensable to humans, rats, and chicks have been found in reasonable quantity. Feeding tests (*94, 237, 238, 401*) have indicated a deficiency of the essential amino acid methionine, but this is not serious as the shortage can be compensated for by including a material containing this amino acid, such as a cereal, or by adding synthetic methionine. It should be pointed out that the inclusion of yeast in the human diet is based chiefly on its value of supplementing the amino acid and vitamin deficiency of cereal grains. It should not be expected to act as the sole source of protein in the diet of either animals or humans.

The nitrogen-containing substances in yeast have been designated as crude protein in recognition of the fact that other nitrogenous constituents are present. About 80 percent of the nitrogen is as amino acids (*401*). On the basis of the total nitrogen, nonprotein constituents have been found as follows: Purines 8 percent, pyrimidines 4 percent, choline 0.5 percent, and glucosamine 0.5 percent (*286*).

Phosphorus is another important constituent of yeast, and averaged about 1.4 percent in 17 samples of dried yeast prepared from citrus waste.[7] This value is in agreement with that obtained from yeast from other sources, but is high in comparison with most feeds. Much of

[7] Unpublished data from the Citrus Products Station (U. S. Dept. Agr.), Winter Haven, Fla., 1955.

the phosphorus is in the form of nucleic acids, and the presence of these compounds is considered as a complicating factor in evaluating yeast as a source of protein.

Yeasts are regarded as good sources of B-vitamins. In one study (*451*) a sample of *T. utilis* produced from citrus press liquor gave the following values: Thiamine 2.8 to 2.9, riboflavin 3.6 to 4.2, niacin 50.4, pantothenic acid 8.4, all expressed as milligrams per 100 gm.; and ergosterol 0.5 percent.

In earlier work on the production of yeast from citrus press liquor, a batch method was used (*322*). Later a continuous process was developed (*451*), in which a nutrient solution prepared from citrus press liquor was fed continuously into an aerated propagator and an equal volume of yeast slurry simultaneously harvested. The average time in the propagator was somewhat less than 3 hours. During fermentation practically all the sugars are consumed. The yield of yeast will vary with the sugar content of the mash, lower sugar contents favoring higher percentage yields based on the amount of sugar present. A 2-percent sugar mash will give a yield of about 40 percent based on the sugar consumed.

Although citrus press liquor is rich in carbohydrates, certain nutrients need to be supplied, particularly nitrogen and phosphorus. Nitrogen can be supplied in the form of ammonia and ammonium sulfate. When the organisms have utilized the ammonia from ammonium sulfate, sulfuric acid remains and serves to control the pH. By varying the ratio of ammonia to ammonium sulfate, the pH of the fermentation can be controlled within reasonable limits. A pH of about 4.0 appears to be the most favorable for growing the yeast. Phosphorus may be supplied as trisodium phosphate. Practically all the nitrogen and most of the phosphorus to be found later in the yeast must be supplied. Approximately 0.36 pound of ammonium sulfate and 0.13 pound of trisodium phosphate must be added for each pound of yeast produced.[8]

Air must be supplied in generous quantities in order to promote rapid yeast growth and minimum alcohol production. Air is introduced at the bottom of the fermenter and passes up through the liquid as fine bubbles. A method commonly used in the baker's yeast industry is to place coils with 1/16-inch holes at the bottom of the fermenter and connect an air-pressure line to the coil. Another method is to introduce air through porous ceramic material in the form of candles or a false bottom in the yeast propagator. In still another procedure air is dispersed by a Waldhof aeration wheel (*201*) or arrowhead turboimpeller (*352*). Less air is required if the bubbles are finely dispersed. The approximate range is from 200 to 500 cubic feet of air per pound of yeast produced.

[8] See footnote 7.

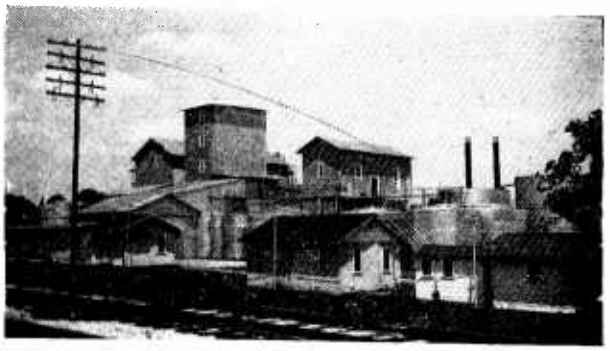


FIGURE 32.—Plant for producing alcohol from citrus waste.

Industrial Alcohol [9]

Oranges, grapefruit, and tangerines contain considerable amounts of sugar, which can be converted to ethyl alcohol by yeast fermentation. Citrus juices have been used for the preparation of alcoholic beverages, such as wines, brandies, and cordials (*460*). Because a slight bitterness remains after sugar removal, dry wines have not found favor, and sweet citrus wines are preferred.

Industrial alcohol can be made from the press liquor obtained in drying citrus waste for feed or from citrus molasses (*457*). Citrus press liquor is too dilute in fermentable sugars to provide a reasonable concentration of alcohol for economical recovery. Citrus molasses may be added to the press liquor until the sugar content is 10 to 12 percent. Frequently citrus molasses is merely diluted with water to the proper concentration. Figure 32 shows a plant where alcohol is made from citrus waste.

No particular difficulties are encountered in the fermentation by yeasts (preferably *Torulopsis utilis*), but the pH of the mash should be adjusted to about 4.0 by the addition of sulfuric acid. Fermentation is complete in 3 days, and about 90 percent of the theoretical yield (45 percent of sugars) has been reported (*322*). Dried yeast can be obtained as a by-product, or the still residues can be concentrated for stock feed. If press juice is used, some peel oils will be found in the alcohol from the rectifying column. Special equipment is needed for removal of this oil prior to fermen-

[9] Anyone contemplating the production of alcohol should first consult the proper authorities in the Alcohol and Tobacco Tax Division, Internal Revenue Service.

tation. Use of citrus molasses eliminates this problem.

Lactic Acid

Lactic acid has been considered from time to time as a possible fermentation product from citrus juices, citrus press liquor, or citrus molasses. Lactic acid is used in certain food products and in the preparation of plastics. Fermentation is easily controlled, because it is conducted at 113° to 131° F., which is too warm for most other fermentations. *Lactobacillus delbrueckii* is a common organism used for lactic acid production. The chief difficulties in fermentation are in the recovery and purification of the acid. Fractional distillation is not possible because of the high boiling point of the acid, and other means of recovery are necessary.

Experiments have been conducted on the production of lactic acid from grapefruit juice (*319, 321*). A starter of naturally occurring organisms was prepared by neutralizing the juice with calcium carbonate and incubating at 122° F. for 2 to 3 days. Approximately 5 percent of the starter was used to inoculate the main batch. The main fermentation was conducted at 122° to 130°, the mash being neutralized periodically with calcium carbonate to keep the pH between 4.0 and 6.5. Fermentation required 6 to 8 days for completion. Sugar utilization was 81 to 92 percent, and the yield of lactic acid amounted to 71 to 84 percent of the sugar fermented.

At the conclusion of the fermentation calcium hydroxide was added until the batch was alkaline to phenolphthalein. The precipitated calcium citrate was removed by filtration, and the filter cake washed with hot water. Combined filtrate and washings were treated with activated carbon, and the mixture again filtered. The filtrate was concentrated to 21° Baumé, and upon standing calcium lactate was crystallized. Additional crystals were obtained by further concentration, and purification was accomplished by recrystallization. Lactic acid was obtained by adding sulfuric acid to the calcium lactate and separating the precipitated calcium sulfate.

Other methods for the recovery and purification of lactic acid have been considered because of the losses incurred in the preceding method. One approach to the problem consists of using ammonia instead of calcium carbonate or hydroxide to neutralize the acid as it is formed during fermentation (*116, 117*). Ammonium lactate remains in solution during fermentation, clarification, and concentration, and is converted into butyl lactate, which is sufficiently volatile to be purified by fractional distillation. In the laboratory an impure solution was evaporated at a pressure of 30 mm. of mercury to a concentration of 71 to 73 percent of ammonium lactate, then butyl alcohol added, and the mixture refluxed for 6½ hours. The vapors escaping were fractionated to recover ammonia, butyl lactate, and alcohol. The alcohol was returned to the system, and the ammonia could be recovered for use in the next fermentation. The butyl lactate was of high purity, and could be marketed as such or hydrolyzed. This method has been investigated on a pilot-plant scale at Lake Alfred, Fla.

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